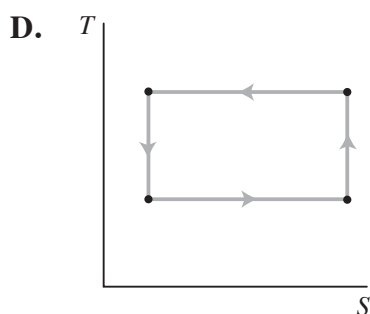
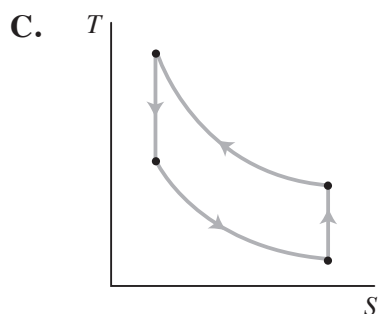
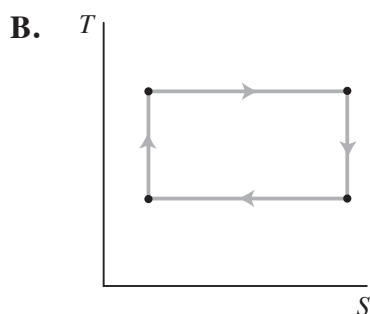
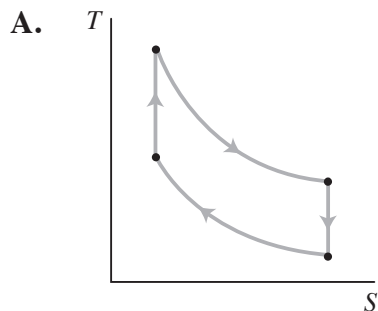


Second Law of Thermodynamics Practice Items

- When a hot stone is dropped into a cool water bath and heat flows from the stone into the bath
 - More entropy is lost in the stone than gained by the water.
 - More entropy is gained by the stone than lost by the water.
 - Less entropy is lost by the stone than gained by the water.
 - The change in entropy in the stone is balanced by an equal and opposite change in entropy in the water.
- Free expansion is an irreversible process in which a gas expands into an insulated evacuated chamber. During a free expansion of an ideal gas
 - the temperature remains constant.
 - the entropy of the gas increases.
 - the internal energy of the gas remains constant.
 - I
 - I and III
 - II and III
 - I, II, and III
- Which of the following statements is NOT true?
 - The Carnot cycle is reversible.
 - The entropy of the universe has increased after a complete Carnot cycle.
 - The Carnot cycle is never 100% efficient.
 - all of the above are true
- Using the key below, which of the following sequences represents either a forward or reverse Carnot cycle?
 - adiabatic expansion
 - adiabatic compression
 - isothermal expansion
 - isothermal compression
 - DD, AA, CC, BB
 - CC, AA, DD, BB
 - BB, DD, AA, CC
 - more than one of the above
- Which of the following does NOT change for an ideal gas undergoing adiabatic compression?
 - entropy
 - internal energy
 - pressure
 - volume
- Which of the following does NOT change for an ideal gas undergoing isothermal compression?
 - entropy
 - internal energy
 - pressure
 - volume
- What is the maximum efficiency of an engine operating between 177 °C and 27 °C?
 - 15%
 - 33%
 - 50%
 - 85%

8. Which of the following graphs represents temperature vs. entropy of the ideal gas serving as the working fluid within a Carnot engine operating in the forward direction?



9. A real-world heat pump in a sun room has a coefficient of performance of 3.0 when the interior temperature is 23°C and the outside temperature is 2°C . How much electrical power is consumed for it to produce 480 watts of heating in these conditions?

- A. 34 W
 B. 63 W
 C. 160 W
 D. 480 W

10. A sealed container holds 1-L of hydrogen gas (H_2) at STP. A second sealed container holds 1-L of helium gas (He) at STP. Both containers are heated isochorically to 100°C . Which gas experiences the greatest change in entropy?

- A. the hydrogen gas
 B. the helium gas
 C. both have equal changes in entropy
 D. the entropy of neither gas changes

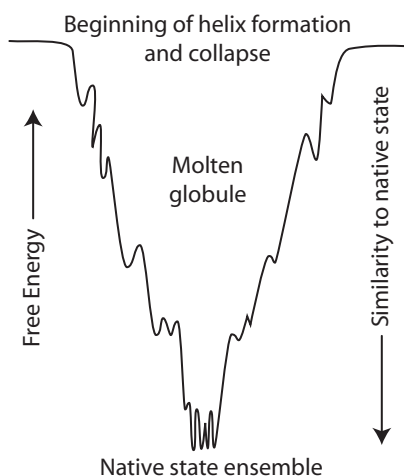
11. What is the relationship between a microstate and a macrostate of a thermodynamic system?

- A. A microstate is a point in phase space, whereas a macrostate describes the relationship of the system to its surroundings.
 B. A microstate corresponds to the quantum electrodynamic parameters of the system, whereas a macrostate describes the system as measured in the laboratory.
 C. A macrostate corresponds to the macroscopic properties of a statistical ensemble comprised of the accessible microstates.
 D. A microstate is defined by specifying external parameters whereas a macrostate is defined as a state for which particle motions are completely specified.

Passage (Questions 12-16)

Conformational entropy is the entropy associated with the physical arrangement of a polymer chain that assumes a compact or globular state in solution. The concept is most commonly applied to biological macromolecules such as proteins and RNA, but can also be used for polysaccharides and other polymeric organic compounds. To calculate the conformational entropy, the possible conformations assumed by the polymer may first be discretized into a finite number of states, usually characterized by unique combinations of certain structural parameters, each of which has been assigned an energy level. In proteins, backbone dihedral angles and side chain rotamers are commonly used as descriptors, and in RNA the base pairing pattern is used. These characteristics are used to define the degrees of freedom in the statistical mechanics sense of a possible microstate. The conformational entropy associated with a particular conformation is then dependent on the probability associated with the occupancy of that state.

The folding funnel hypothesis is a specific version of the energy landscape theory of protein folding, which assumes that a protein's native state corresponds to the global free energy minimum under the solution conditions usually encountered in cells. Although energy landscapes may be "rough", with many non-native local minima in which partially folded proteins can become trapped, the folding funnel hypothesis assumes that the native state is a deep free energy minimum with steep walls, corresponding to a single well-defined tertiary structure.



In the canonical depiction of the folding funnel, the depth of the well represents the energetic stabilization of the native state versus the denatured state, and the width of the well represents the number of possible conformations assumed by the protein. The surface outside the well is shown as relatively flat to represent the heterogeneity of the random coil state.

The entropy of heterogeneous random coil or denatured proteins is significantly higher than that of the folded native state. In particular, the conformational entropy of the amino acid side chains in a protein is thought to be a major contributor to the stabilization of the denatured state and thus a barrier to protein folding. However, a recent study has shown that side-chain conformational entropy can stabilize native structures among alternative compact structures. The conformational entropy of RNA and proteins can be estimated; for example, empirical methods to estimate the loss of conformational entropy in a particular side chain on incorporation into a folded protein can roughly predict the effects of particular point mutations in a protein. Side-chain conformational entropies can be defined as Boltzmann sampling over all possible rotameric states. If a system can be in states n with probabilities P_n

$$S = -k_B \sum_{n=1}^W P_n \ln(P_n)$$

where k_B is Boltzmann's constant and W is the number of possible conformations.

It has been proposed that decreasing the conformational flexibility of the unfolded chain (by substitution with proline, or by replacement of glycine) should lead to an increase in the stability of the folded relative to the unfolded protein. The limited conformational range of proline residues lowers the conformational entropy of the denatured state and thus increases the free energy difference between the denatured and native states. A correlation has been observed between the thermostability of a protein and its proline residue content.

12. When the temperature of a dilute aqueous solution containing globular proteins is increased from 29°C to 32°C, the conformational entropy of the suspended polypeptides
- A. decreases
 - B. remains the same
 - C. increases
 - D. becomes less predictable
13. Based on the information presented in the passage, for a protein complex with a ligand-binding interface, point mutations downstream from the binding site that increase conformational entropy are most likely
- A. to decrease protein-ligand binding affinity.
 - B. to increase protein-ligand binding affinity.
 - C. not to alter protein-ligand binding affinity.
 - D. to increase catalytic efficiency.
14. In the folding funnel hypothesis, the width of the well in the diagram increases with
- A. conformational entropy
 - B. free energy
 - C. intramolecular hydrogen bonding
 - D. protein solubilization
15. A theoretical polymer with only one possible conformation would
- A. have zero conformational entropy.
 - B. possess conformational entropy equal to k_B .
 - C. be at absolute zero, 0-K, temperature.
 - D. have conformational entropy due to possible states of translational momentum.
16. A mutation substituting two proline residues downstream from the active site of an enzyme reduced enzyme activity. These substitutions also eliminated a hydrogen bond and some hydrophobic interactions suggesting that
- A. those factors outweighed the decrease in conformational stability.
 - B. the substitutions increased the conformational entropy of the native protein.
 - C. these factors altered the shape of the binding site.
 - D. the conformational flexibility of the unfolded chain was increased.
-

Second Law of Thermodynamics

Answers and Explanations

1. C

The temperatures of the stone and bath are changing as heat flows, so the mathematical expression of the idea would be more complicated than below, but to get the basic idea we can look to the entropy change for heat flow in a reversible process. The higher the temperature, the less entropy change occurs with a given amount of heat flow.

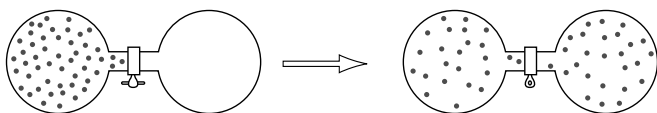
$$\Delta S = \frac{Q_r}{T}$$

ΔS = entropy change
 Q_r = heat flow (in reversible process)
 T = temperature

As heat flow occurs from the hot stone into the cold water, the water gains entropy and the stone loses entropy as thermal energy increases and decreases respectively. However, because the stone is a higher temperature than the water, as predicted in the formula above, the amount of entropy lost by the stone for the same amount of heat flow is less than the amount of entropy gained by the water. Put it together and the entropy of the universe is increasing, which is why the heat flow is spontaneous.

2. D

Free expansion can be observed in the apparatus below when the stopcock is opened between two bulbs connected by a tube. In the initial state, all of the gas (N particles) is constrained to occupy the bulb on the left. The bulb on the right contains a vacuum. When the stopcock is opened, the gas spontaneously moves to occupy both bulbs.



Choice I and III are correct for the same reason. No heat flow occurs, and no work is done when the stopcock is opened and the gas expands to fill the vacuum. If there is no heat flow and no thermodynamic work there is no internal energy change.

$$\Delta U = Q - W$$

And with an ideal gas where thermal energy is the only form of internal energy, if there is no internal energy change, the temperature must remain constant.

$$U = \frac{3}{2}nRT$$

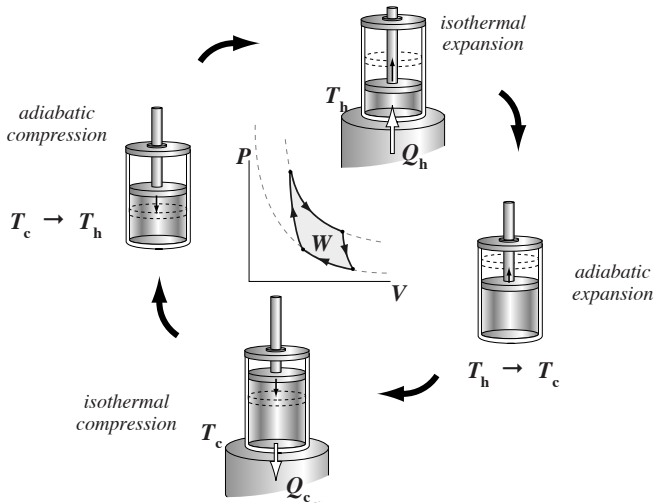
Choice II is also correct. In the initial state, all of the gas (N particles) is constrained to occupy a single bulb. When the stopcock is opened, the gas spontaneously moves to occupy both bulbs. In this example, with the stopcock opened, the probability of the second state is 2^N times that of the initial state. The entropy has increased proportional to the logarithm of this increased probability.

3. B

The Carnot cycle consists of four stages: an isothermal expansion on the hot sink, an adiabatic expansion, an isothermal compression on the cold sink, and lastly an adiabatic compression. Each of these stages is reversible. Because each stage individually doesn't increase the entropy of the universe, neither does the complete cycle. The Carnot cycle is the ideal theoretical cycle. It does not increase the entropy of the universe. The Carnot cycle allows us to define the minimum amount of heat which must be delivered to the cold sink, in other words, the amount of heat that isn't available to be converted into work. The Carnot cycle represents the boundary between possible and impossible engines, between a spontaneous engine that runs forward and increases the entropy of the universe and an impossible engine that would cause the entropy of the universe to decrease.

4. D

All three choices represent either a forward or reverse Carnot cycle. (In the reverse Carnot cycle, work is done to extract heat from the cold sink and expel it into the hot sink.)



5. A

The entropy doesn't change for the system through an adiabatic expansion or compression. Although the temperature does increase, for example, in the case of an adiabatic compression, the volume decreases, and the two effects balance each other with respect to entropy change. An adiabatic compression is isentropic, in other words.

6. B

An isothermal compression is one in which the temperature does not change. The internal energy is only thermal energy, ie. the kinetic energy of the particles, with an ideal gas, so the internal energy goes up or down with the temperature. If the temperature is constant so is the internal energy.

$$U = \frac{3}{2}nRT$$

It should be noted that even though the entropy of the gas decreases as heat flows out into the surroundings during an isothermal compression and its volume decreases, the surroundings experience an entropy increase of exactly the same magnitude, being the same temperature, so even though the entropy of the system changes in an isothermal compression, the entropy of the universe does not change, so like the adiabatic compression, an isothermal compression is also reversible.

7. B

The Carnot efficiency describes the maximum possible amount of heat input that can be transformed into work for a given engine.

$$\epsilon = \frac{W}{Q_h} = 1 - \frac{T_c}{T_h}$$

A key with this problem is to remember to convert the temperature values from Celsius to Kelvin ($K = ^\circ C + 273$).

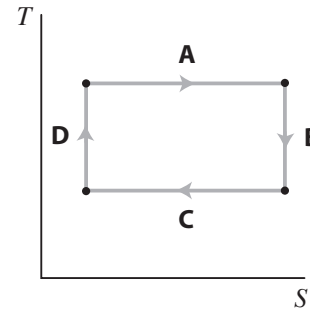
$$T_c = 27^\circ C = 300 \text{ K}$$

$$T_h = 177^\circ C = 450 \text{ K}$$

$$\epsilon = 1 - \frac{300 \text{ K}}{450 \text{ K}} = 33\%$$

8. B

Each stage on the figure below represents a stage in the forward Carnot cycle.



A – Isothermal expansion on the hot sink

B – Adiabatic expansion

C – Isothermal compression on the cold sink

D – Adiabatic compression

9. C

A heat pump is a heat engine operating in reverse. A heat pump applies work to extract heat, Q_c , from a cold sink and delivering a larger amount of heat, Q_h , to a hot sink. ($Q_h = Q_c + W$). The coefficient of performance, COP, of a heat pump is the ratio of the heat delivered to the hot sink to the work required to transfer the heat.

$$\text{COP} = \frac{Q_h}{W}$$

W is the energy purchased from the power company.
 Q_h is the heating delivered to the home.

$$3 = \frac{480 \text{ W}}{W}$$

$$W = 160 \text{ W}$$

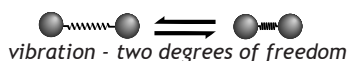
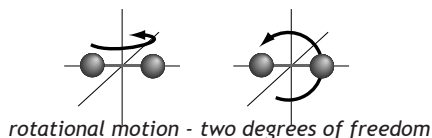
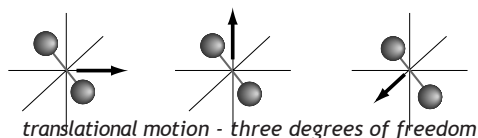
To deliver 480 W of heating, the homeowner must supply 160 W of electrical power to his real world heat pump.

Note that if the heat pump were working ideal Carnot efficiency, its COP would be greater. We didn't need the given temperatures to answer the particular question asked, but after converting them into Kelvin ($\text{K} = ^\circ\text{C} + 273$), we can determine the Carnot COP.

$$\begin{aligned} \text{COP}_{\text{Carnot}} &= \frac{T_h}{T_h - T_c} \\ &= \frac{296\text{K}}{296\text{K} - 275\text{K}} \\ &= 14.1 \end{aligned}$$

10. A

With the ability to store energy in both vibrational and rotational modes, a diatomic gas like H_2 has more partitions for thermal energy. As a sample of diatomic gas takes in heat, the energy spreads out into all of its degrees of freedom. H_2 has a higher molar heat capacity than He.



Because it has a higher molar heat capacity, more heat flow into the H_2 sample will occur than into He to obtain the same temperature change. Although the expression demonstrating the entropy change over the temperature change would require calculus, it's easy to see that it would be greater for H_2 . A greater amount of heat flow corresponds to a greater entropy change.

$$\Delta S = \frac{Q_r}{T} \quad \begin{array}{l} \Delta S = \text{entropy change} \\ Q_r = \text{heat flow (in reversible process)} \\ T = \text{temperature} \end{array}$$

Another way to understand why H_2 will have greater entropy at a given temperature than He is visualized in the degrees of freedom pictured above. Because H_2 has rotational and vibrational degrees of freedom in addition to translational, at a given temperature the macrostate of H_2 supervenes on a much larger ensemble of microstates. There are a great many more combinations for the distribution of thermal energy with H_2 among its degrees of freedom than with He.

11. C

A microstate is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuations. Think of a microstate as a snapshot of every particle at a moment in time. In contrast, the macrostate of a system refers to its macroscopic properties, such as its pressure, volume, and temperature. Microstates appear as different possible ways the system can achieve a particular macrostate. In other words, a macrostate is characterized by a probability distribution of possible states across a certain statistical ensemble of all microstates.

Entropy rises with the multiplicity of the system (the number of possible microstates that correspond to a particular macrostate).

$$S = k \ln X \quad \begin{array}{l} S = \text{entropy} \\ k = \text{Boltzmann's constant} \\ X = \text{multiplicity} \end{array}$$

12. C

The vibrational and rotational kinetic energy of the various groups within the protein increase with temperature, and the conformational space explored grows. As the protein transitions to the unfolded state the number of conformations underlying the state of the protein increases exponentially.

13. A

Although the passage mentions the possibility of exceptions, the passage makes the arguments and presents evidence supporting the conclusion that increases in conformational flexibility in distant groups will stabilize an unfolded protein. This will decrease the possibility of an ordered binding site, so the changes proposed should lead to a decrease in protein-ligand binding affinity.

14. A

The passage describes the width of the well as representing the number of possible conformations assumed by the protein. The conformational entropy of a state increases with the number of conformations underlying it.

15. A

Conformational entropy is defined in the passage as the entropy associated with the physical arrangement of the polymer chain. If there is only one possible configuration, the conformational entropy would be zero. The entropy value returned by Boltzmann sampling as described by the formula in the passage would be zero ($\ln(1) = 0$).

$$S = -k_B \sum_{n=1}^W P_n \ln(P_n)$$

There may be other forms of entropy such as those involving degrees of freedom in translational motion, hydration or crystal packing, for example, but conformational entropy would be zero.

16. C

The discussion in the passage of the effects of proline substitutions to stabilize the native state of a globular protein were focused on the decrease in the conformational entropy of the unfolded state. Changes that increase the enthalpy of the native state, even if they decrease the entropy of the unfolded state, might make an ordered active site less likely and decrease enzyme activity.

