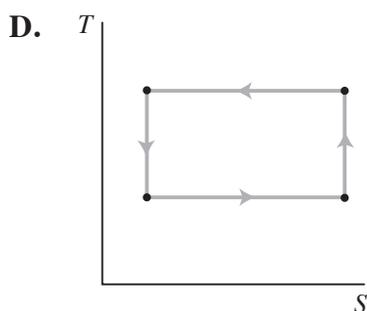
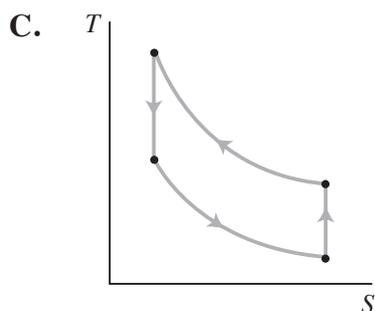
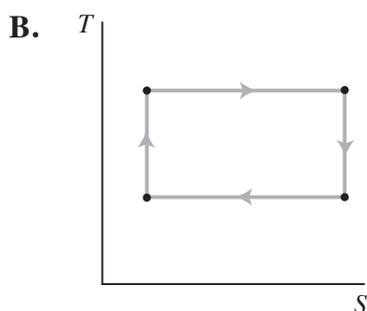
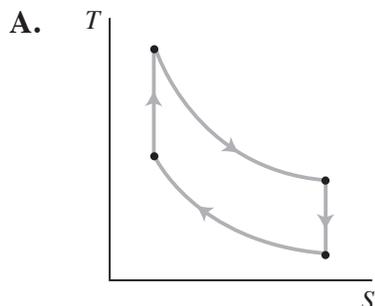


## Second Law of Thermodynamics Practice Items

- 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  $23^{\circ}\text{C}$  and the outside temperature is  $2^{\circ}\text{C}$ . 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 ( $\text{H}_2$ ) at STP. A second sealed container holds 1-L of helium gas ( $\text{He}$ ) at STP. Both containers are heated isochorically to  $100^{\circ}\text{C}$ . 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

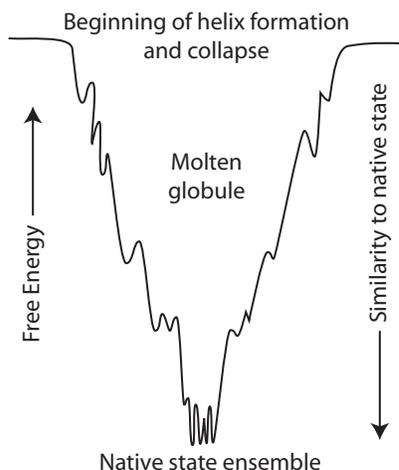
11. What is the relationship between a microstate and a macrostate of a thermodynamic system?

- 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.
-