***Chemistry***

**16: Thermodynamics**

**16.2: Entropy**

7. In Figure 16.8, all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, Δ*S*, for the system when it is converted from distribution (b) to distribution (d).

Solution

There are four initial microstates and four final microstates.



9. Consider a system similar to the one in Figure 16.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to . What does this comparison tell us about even larger systems?

Solution

A system of N particles will have 2N microstates, since each of the particles can be in one of the two states (on the left or on the right), and its probability to be in one of them is independent of positions of the other particles. Therefore, there are 26 = 64 possible microstates for six particles. Only two of them correspond to all the particles being in one box (one for the right box and one for the left box). Thus, the probability for all the particles to be on one side is . This probability is noticeably lower than the  result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

11. Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

Solution

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.



13. At room temperature, the entropy of the halogens increases from I2 to Br2 to Cl2. Explain.

Solution

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I2 is a solid, Br2 is a liquid, and Cl2 is a gas.

15. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) C2H5OH(*l*) or C3H7OH(*l*)

(b) C2H5OH(*l*) or C2H5OH(*g*)

(c) 2H(*g*) or H(*g*)

Solution

(a) C3H7OH(*l*) as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) C2H5OH(*g*) as it is in the gaseous state. (c) 2H(*g*), since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

17. Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

(a) 

(b) 

(c) 

Solution

(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

19. Write the balanced chemical equation for the combustion of benzene, C6H6(*l*), to give carbon dioxide and water vapor. Would you expect Δ*S* to be positive or negative in this process?

Solution



There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and Δ*S* is positive.

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