Section 71 – Entropy

71-1. Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $H_2(g)$, $HBrO_4(g)$, $HBr(g)$

(b) $H_2O(l)$, $H_2O(g)$, $H_2O(s)$

(c) $He(g)$, $Cl_2(g)$, $P_4(g)$

Solution

(a) $H_2(g) < HBr(g) < HBrO_4(g)$, due to increasing complexity and mass of molecules;

(b) $H_2O(s) < H_2O(l) < H_2O(g)$ due to increasing dispersal of matter;

(c) $He(g) < Cl_2(g) < P_4(g)$ due to increasing complexity and mass of species

71-2. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. 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, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

71-3. Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$I_2(s) \rightarrow I_2(g)$

$I_2(s) \rightarrow I_2(l)$

Is ΔS positive or negative in the processes? In which of the processes will the magnitude of the entropy change be greater?

Solution

The change of entropy will be positive in the both cases, as a relatively ordered solid is converted into less ordered liquid or gas. The sublimation will lead to a greater change in S since the final state (gas) is more disordered and dispersed than liquid.

71-4. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $C_2H_5OH(l)$ or $C_3H_7OH(l)$

(b) $C_2H_5OH(l)$ or $C_2H_5OH(g)$

(c) $2H(g)$ or $H(g)$

Solution

(a) $C_3H_7OH(l)$ 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) $C_2H_5OH(g)$ 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).

71-5. Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.

(b) Exhaled breath forms fog on a cold morning.

(c) Snow melts.

Solution

(a) $\Delta S > 0$; entropy increases since water molecules in the solid possess greater freedom of motion at the higher temperature.

(b) $\Delta S < 0$; the fog is comprised of tiny water droplets formed by condensation of water vapor in the exhaled breath, and entropy decreases as the water first cools from body temperature to colder ambient temperature and then transitions from the gaseous to the liquid state.

(c) $\Delta S > 0$; entropy increases as the water molecules in the solid snowflakes gain greater freedom of motion upon melting to yield liquid water.

71-6. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $Na^+(aq) + Cl^-(aq) \longrightarrow NaCl(s)$

(b) $2Fe(s) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_2(s)$

(c) $2C_6H_{14}(l) + 19O_2(g) \longrightarrow 14H_2O(g) + 12CO_2(g)$

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.

71-7. The balanced chemical equation for the combustion of methane, $CH_4(g)$ is as follows:

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

Solution: With three moles of gaseous reactants and three moles of gaseous products, it is not clear if the products or reactants have the greater entropy.

71-8. The balanced chemical equation for the combustion of benzene, $C_6H_6(l)$ is as follows:

$$C_6H_6(l) + 7.5\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(g).$$

Would you expect ΔS 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 ΔS is positive.