Answers to Exercise 6.2
Entropy and Microstates

1. The standard enthalpy of formation and standard free energy of formation are both defined as zero for a pure element in the standard state at 25 °C.

   Entropy is defined differently. The entropy of a pure element is zero when it is in a perfect crystal at 0 K (-273.15 ℃). Since entropy increases with temperature, when the pure element is at 25 °C, its entropy is higher than zero.

2.

(a) $S = k_B ln\Omega = k_B ln(9)$

There are nine possible microstates:

- Jar A = 8 marbles, Jar B = 0 marbles
- Jar A = 7 marbles, Jar B = 1 marble
- Jar A = 6 marbles, Jar B = 2 marbles
- Jar A = 5 marbles, Jar B = 3 marbles
- Jar A = 4 marbles, Jar B = 4 marbles
- Jar A = 3 marbles, Jar B = 5 marbles
- Jar A = 2 marbles, Jar B = 6 marbles
- Jar A = 1 marble, Jar B = 7 marbles
- Jar A = 0 marbles, Jar B = 8 marbles

(b) $S = k_B ln\Omega = k_B ln(5^2) = k_B ln(25)$

Now, it is necessary to consider the colours of the marbles in each jar. There are $5^2 = 25$ possible microstates for this system.

This is because there are five different ways to distribute the red balls and also five different ways to distribute the blue balls. Since every red distribution can be combined with every blue distribution, there are $5 \times 5 = 5^2 = 25$ possible microstates.

A sample microstate is:

- Jar A = 1 red marble/1 blue marble, Jar B = 3 red marbles/3 blue marbles

(c) Yes. While the number of marbles was the same, having to discriminate between red and blue marbles increased the entropy of the system by increasing the number of “available microstates”.

3.

(a) The density of a gas is substantially less than the density of a solid or liquid. The particles are distributed over a much larger volume (per mole) and, as such, there is a much larger number of possible positions for each particle relative to the same mass in solid or liquid state. This means that there are many more possible microstates for the positions of the particles in the gas phase.

Since entropy increases with the number of possible microstates and producing more gas particles increases the number of possible microstates, producing more gas particles increases entropy.

(b) As we discussed in CHEM 1000, ionic lattices are highly ordered systems. Dissolving an ionic solid in water breaks up the ionic lattice, significantly increasing the number of possible positional microstates for the ions.

(c) If the ions increase the order of the water molecules in the sample (relative to pure water) by a large enough amount, that can decrease the entropy of the system. This would be a result of the water molecules being "organized" around the ions in hydration spheres.

Recall that in CHEM 1000, we discussed aquaions like $[Fe(OH_2)_6]^{3+}$. *There are actually more layers of water around the ion than just the initial one described by that formula.*

It is worth remembering that the ions are not totally free to disperse anywhere in the solution. Cations and anions will generally stay near enough each other that no large pockets of positive (or negative) charge build up. Nevertheless, the loss of order from breaking up the ionic lattice is usually a larger effect than any organization of water molecules so, most of the time, dissolving an ionic solid in water is favoured by entropy.