T-7. Entropy: Other Topics

Part 1: Entropy with Calorimetry

Solutions to Dicussion Questions (Part 1)

1. The melting point of lead is 327.5°C. To melt one kilogram of lead at this temperature, you must add about 25,000 J of heat. When you do this, does the entropy of the lead change? (See if you can answer based on the qualitative idea of "order vs. disorder.")

The entropy of the lead increases. Intuitively, a solid is "more ordered" than a liquid. In a solid, the particles have more structure, perhaps even an orderly crystal structure. The particles in a liquid, on the other hand, have much less structure. So if entropy measures the amount of disorder in a system, and we turn something from an orderly solid into a disorderly liquid, then we are certainly adding entropy.

Apart from this, we know from the formula dS = dQ/T that *whenever* we add heat to a system, we increase its entropy.

2. In Discussion Question 3 above, if you said that the entropy of the system changes, then by how much? (Give a numerical answer.)

Let us assume that the melting is done reversibly. Then the entropy change associated with each bit of added heat is dS = dQ/T. We can integrate this from the beginning of the process to the end of the process to find ΔS. Note however that since the entire process takes place at one temperature (T = 327.5^{0}C), the T comes out of the integral and we get ΔS = Q/T = 25,000 J / 600.65 K = 41.6 J/K.

Note that since the entropy change depends only on the initial and final states, our answer is correct even if the process was carried out in an irreversible way.

Answers to Problems (Part 1)

1. **a)** *Less* than 2 T

b) T_f = 1.4 T

c) $\Delta S_{small} = -Mc_L \ln \frac{15}{7}$

d) $\Delta S_{big} = 4Mc_L \ln \frac{7}{5}$

e) $\Delta S_{sys} \approx 0.58\, Mc_L$

2. $T_L \geq 224^0C$

3. a) $T_f = \dfrac{M_L c_L T_L + M_{ice} c_{ice} T_{ice} - M_{ice} L_f^{H_2O}}{M_L c_L + M_{ice} c_w}$ for temperatures in celsius

b) $\Delta S_{bowl} = M_L c_L \ln \dfrac{T_f}{T_L}$ (negative)

c) $\Delta S_{ice} = M_{ice} c_{ice} \ln \dfrac{273K}{T_{ice}} + \dfrac{M_{ice} L_f^{H_2O}}{273K} + M_{ice} c_w \ln \dfrac{T_f}{273K}$ (positive)

d) The total change in entropy will be *positive*, since this is an irreversible process.

e) $\Delta S_{sys} = M_L c_L \ln \dfrac{T_f}{T_L} + M_{ice} c_{ice} \ln \dfrac{273K}{T_{ice}} + \dfrac{M_{ice} L_f^{H_2O}}{273K} + M_{ice} c_w \ln \dfrac{T_f}{273K}$ (positive)

Part 2: Microstates

Solutions to Dicussion Questions (Part 2)

1. Entropy is sometimes said to be a 'measure of disorder.' Why are systems that are 'disordered' said to be more entropic than systems that are 'ordered'? Hint: Consider your room. Each item in your room can be placed anywhere in the room. How does the number of ways for the room to be 'disordered' (messy) compare to the number of ways that your room to be 'ordered' (clean)?

More entropic systems are systems where the possible number of microstates that the system can be in is higher, due to $S = k_B \ln \Omega$. In a complex system, there are comparitively few ways for things to be 'ordered', while there are an enormous number of ways for the system to be 'disordered'.

2. Consider a system of N coins, each of which can land on heads (H) or tails (T) when flipped.

a) How many microstates are there in the flipped-coin system?

Each coin can be in one of two possible states (heads or tails). If there are N coins, then there are a total of $\Omega = 2^N$ possible microstates.

b) Suppose the coins are unweighted, so that the odds of a particular coin landing on heads are the same as the odds of that coin landing on tails. What is the probability for landing on a particular microstate? What is the entropy of this flipped-coin system?

Since there are 2^N microstates, each with an equal probability of occurring, then the probability for landing on any particular microstate is $p = 1/\Omega = 2^{-N}$. Since each microstate has an equal probability, we can use the formula $S = k_B \ln\Omega = k_B \ln 2^N$, so $S = Nk_B \ln 2$.

c) Suppose all of the coins are double-head coins, so that each coin will invariably land on heads when flipped. What is the entropy of this flipped-coin system?

There is only one possible microstate here: Every coin lands on Heads. Therefore, $\Omega = 1$ and so the entropy $S = 0$.

d) What is the entropy of the flipped-coin system if the first (N-1) are known to land on heads?

Since we know that the first (N-1) coins are heads, there are only two microstates: all heads and the first (N-1) coins being heads and the last coin being tails. Both microstates are equally likely, so $S = k_B \ln 2$.

e) What is the entropy of the flipped-coin system if at least (N-1) coins are known to land on heads?

This situation is different from the situation from part (d) because now we know that (N-1) coins are heads, but we don't know *which*coin potentially isn't. There is one microstate where *all* coins are heads, and there are N microstates that have (N-1) heads and one tail (one microstate for each coin that could be a tail). Therefore, the entropy is $S = k_B \ln (N+1)$.

3. Entropy is sometimes said to be a measure of *ignorance* about a system. Why are systems that we know everything about less entropic than systems we know nothing about?

As the coin example from Discussion Question 2 illustrates, the more we know about a system, the fewer possible microstates there are. We started knowing nothing about the system, so any outcome was possible. As we learn more, we get constraint on the possible microstates, so the number Ω decreases, decreasing the entropy.

4. Prove that in the case where we have Ω microstates, and the probability for each microstate, p_i, is *equal*, then the formula $S = - k_B \sum p_i \ln(p_i)$ reduces to $S = k_B \ln\Omega$.

If we have Ω microstates and equal probabilities for each microstate, then $p_i = 1/\Omega$, since the sum of the probabilities has to be 1. The product $p_i \ln(p_i)$ becomes $(1/\Omega) \ln (1/\Omega) = (-1/\Omega) \ln \Omega$. We sum this over all Ω microstates, so $S = -k_B\, \Omega\, (-1/\Omega) \ln \Omega = k_B \ln \Omega$, as claimed!

Answers to Problems (Part 2)

1.