# CHEM 361A - Lecture 7 Activity
### Entropy

## In Class

1. Make the following table and fill in everything:

Table 1: Calculating entropy.

| | Reversible | Irreversible |
|---|---|---|
| $\Delta S_{sys}$ | $\frac{q_{rev}}{T}$ | $\frac{q_{rev}}{T}$ |
| $\Delta S_{surr}$ | $-\frac{q_{rev}}{T}$ | $-\frac{\Delta H}{T}$ or $-\frac{\Delta H}{T}$ |

$$\Delta S_{Tot} = \Delta S_{sys} + \Delta S_{surr}$$

2. According to the second law of thermodynamics, the entropy of an irreversible process in an isolated system must always increase. On the other hand, it is well known that the entropy of living systems remains small. For example, the synthesis of highly complex protein molecules from individual amino acids is a process that leads to a decrease in entropy. Is the second law invalid for living systems? Explain.

3. Examining the hydrophobic effect is another way to look at the importance of quantifying the entropy of the system and the surroundings. Pretend that you have a well mixed system of water and a protein with both hydrophobic and hydrophilic groups in an isolated container.
   (a) Does the entropy of the protein go up or down if it were to aggregate? Why?
   (b) Does the entropy of the water go up or down if the protein aggregates? Why?
   (c) How is this generalisable to other non-polar/water interactions (say oil and water)?

4. The second law of thermodynamics asserts that

   > It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equal amount of work by the system on the surroundings.

   This is because the entropy decrease in the hot reservoir must be offset by an increase in entropy in a cold reservoir. What this means is that there is a thermodynamic limit to the efficiency of a heat engine as some heat must be deposited into a cold reservoir.

   (a) To demonstrate why there must be a cold reservoir, determine the work that is performed by the Carnot Cycle when the cold reservoir is at the same temperature as the hot reservoir.

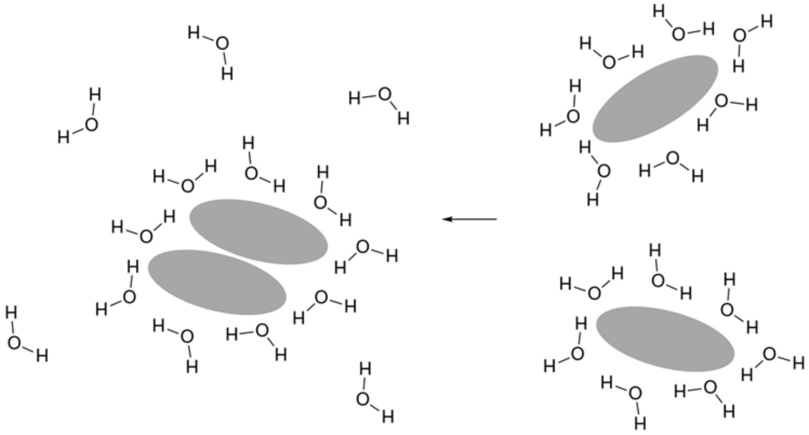


Figure 1: Illustration of protein aggregation.

$q$ ?

(b) Using the labels in Figure 2, determine the $\Delta S_{hot}$, $\Delta S_{cold}$ and $\Delta S_{Total}$.

(c) The maximum efficiency for an ideal Carnot Engine occurs when $\Delta S_{Total} = 0$. Using this condition, write an expression for $|q'|/|q|$.

(d) If the efficiency of a process is the work done over the heat supplied, show that the efficiency of an ideal Carnot Engine is

$$\eta = 1 - \frac{T_{cold}}{T_{hot}}$$

$$\Delta S_{Hot} = \frac{-|q|}{T_{Hot}}$$

$$\Delta S_{cold} = \frac{|q'|}{T_{cold}}$$

$$\Delta S_{tot} = \Delta S_{Hot} + \Delta S_{cold}$$

$$0 = \frac{|q'|}{T_{cold}} - \frac{|q|}{T_{Hot}}$$

$$\frac{|q'|}{T_{cold}} = \frac{|q|}{T_{Hot}}$$

$$\boxed{\frac{|q'|}{|q|} = \frac{T_{cold}}{T_{Hot}}}$$

$$\eta = \frac{|w|}{|q|} = \frac{|q| - |q'|}{|q|}$$

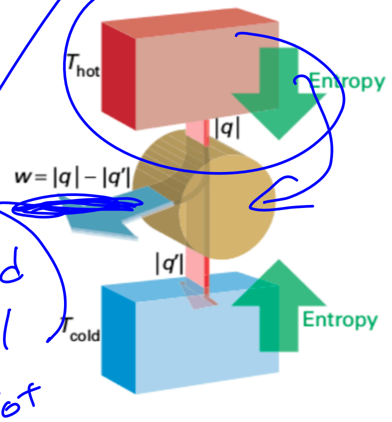


Figure 2: A Carnot Engine connected to a hot and cold reservoir showing the decrease in entropy in the hot reservoir and the increase in entropy in the cold reservoir.

$$= \frac{|q|}{|q|} - \frac{|q'|}{|q|}$$

$$= 1 - \frac{T_{cold}}{T_{Hot}}$$

# Homework

5. Consider the reaction

$$\mathrm{N_2(g) + O_2(g) \longrightarrow 2\,NO\,(g)}$$

   Calculate the values of $\Delta_r S^\circ$ for the reaction mixture, the surroundings, and the universe (total $\Delta S$) at 298 K. Why is your result reassuring to Earth's inhabitants? ($\Delta S_{univ} = -582$ J K$^{-1}$).

6. Calculate the entropy change when neon at 298 K and 1 atm in a container of volume 0.780 L is allowed to expand to 1.25 L and simultaneously heated to 358 K. Assume ideal behaviour. Hint: Because S is a state function, you can first calculate the value of $\Delta S$ for the expansion at constant temperature, and then the value of $\Delta S$ due to heating at constant volume. ($\Delta S_{Tot} = 0.20$ J K$^{-1}$)

7. The second law of thermodynamics requires a particular direction of time since the entropy of an isolated system can never decrease. For this reason, we can use entropy to distinguish the past from the future. For example, we expect in most cases that two substances will mix as time moves forward. We will use the second law of thermodynamics to show this to be true. Suppose we have an isolated container separated in half by a wall. In one half is one mole of gas A, and in the other is one mole of gas B. We can use the fraction of the volume of the box that each gas occupies as a proxy for the number of microstates.

   (a) Using

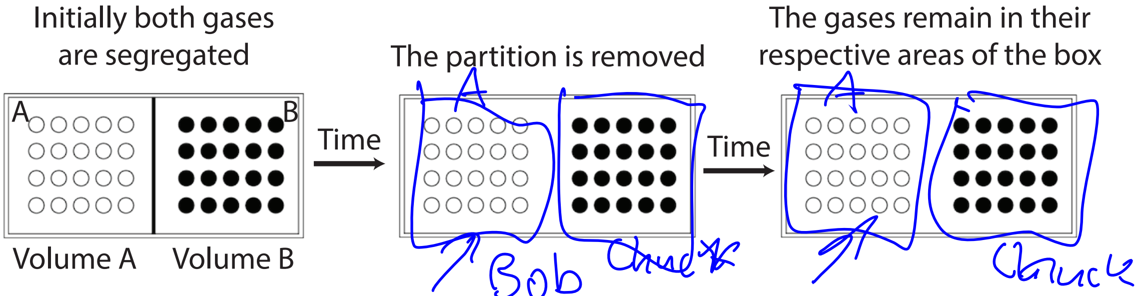
$$\Delta S = nR \ln \frac{V_f}{V_i}$$

   calculate the change in entropy between the case where the partition is first removed and at some later time where all of gas A is found in the same half as it was initially, and all of gas B is found in the same half as it was initially. This is illustrated in Figure 3a. ($\Delta S = 0$)

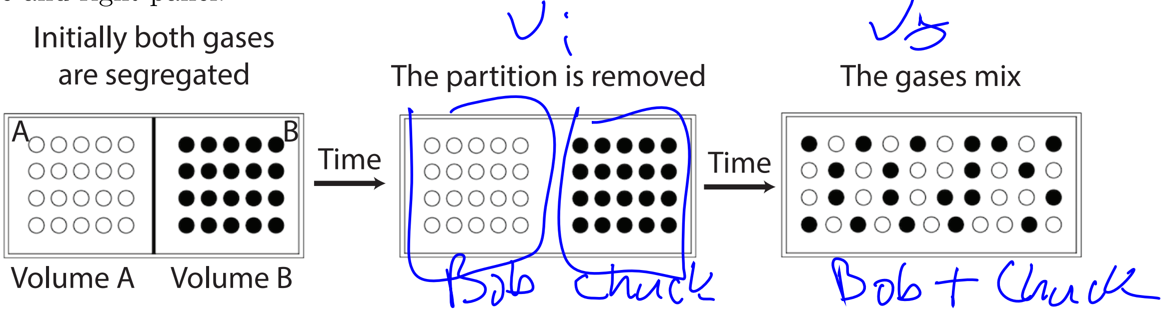
   (b) Now calculate the total change in entropy between when the wall is first removed and at some later time where both gases mixed and filled the total container. This is illustrated in Figure 3b. ($\Delta S = nR \ln \frac{(V_A+V_B)^2}{V_A V_B}$)

   (c) Which scenario (gases stay in the same half of the box or mix and fill the complete volume) will spontaneously occur according to the $\Delta S$ results? Does this fit with your perception of the evolution of time for this system? What about the other scenario: does it fit with time moving forward or time standing still?

$\Delta S_T = 0$ $\qquad \Delta S_A = nR \ln \frac{V_f}{V_i} = nR \ln \frac{Bob}{Bob}$



(a) No gas mixing scenario. We would perceive that very little or no time has passed between the middle and right panel.



(b) Gas mixing scenario. We would expect some measurable amount of time to have passed between the middle and right panel.

Figure 3: Two gas mixing scenarios where the difference in entropy from the middle panel to the right panel can be calculated to demonstrate how entropy is time's arrow.

$$\Delta S_A = nR \ln \frac{B+C}{Bob}$$

$$\Delta S_B = nR \ln \frac{B+C}{Chuck}$$

$$\Delta S_T = \Delta S_A + \Delta S_B = nR \left[ \ln \frac{B+C}{B} + \ln \frac{B+C}{C} \right]$$