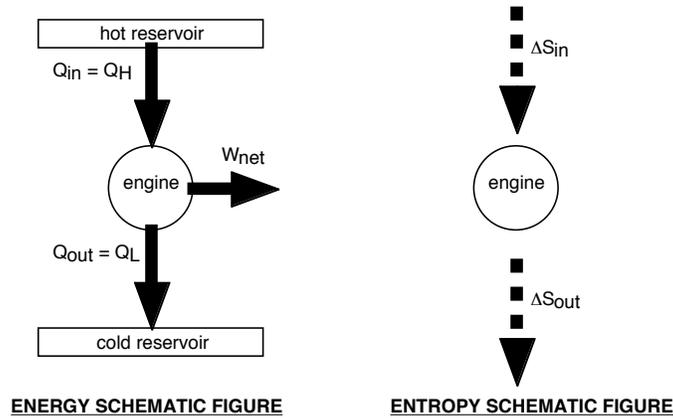# T-6. Entropy and the Second Law

Solutions to Dicussion Questions (Part 1)

1. Shown below are schematic figures for the energy flow and entropy in a heat engine.

ENERGY SCHEMATIC FIGURE   **ENTROPY SCHEMATIC FIGURE**

a) What is the relation between ΔS_{in} and ΔS_{out}? Why is it not possible to develop a cyclic engine that converts heat entirely into work? Why <u>must</u> some heat (Q_{out}) be ejected from the system?

     After a complete cycle, the gas ends up in the same state it began in. So, since entropy is a state function, the net change in entropy over a complete cycle must be zero. Another way of saying this is that you can't be adding or subtracting any net entropy to the gas over a cycle. In other words, the input entropy and the output entropy over a cycle have to be the same: $\Delta S_{in} = \Delta S_{out}$.

     Now, since heat is taken in ($Q_{in} > 0$), we must have $\Delta S_{in} > 0$. Thus $\Delta S_{out} > 0$ as well, and so $Q_{out} > 0$. In other words, some heat must be ejected from the system. For as we see, if all of the input heat were converted into work, then there would be no heat ejected, and this would require a net entropy increase over the cycle, which cannot happen.

b) In a Carnot engine, Q_{in} enters the system only along the isotherm T_H, and Q_{out} leaves the system only along the isotherm T_L. Use your result of (a) to find Q_{out}/Q_{in} in terms of T_H and T_L.

     For the Carnot cycle, all of the input heat enters the system at the same temperature. This allows us to write

$$\Delta S_{in} = Q_{in}/T_H.$$

     Likewise, all of the output heat leaves the system at the same temperature. So we also have

$$\Delta S_{out} = Q_{out}/T_L.$$

But since $\Delta S_{in} = \Delta S_{out}$., this means

$$Q_{in}/T_H = Q_{out}/T_L \,,$$

and hence $Q_{out}/Q_{in} = T_L/T_H$ as desired.

c) An efficient engine converts as much heat as possible into work, ejecting as little as possible. Can you explain why a Carnot cycle gives the greatest possible efficiency? [Hint: Q_{in} enters the system only at the highest temperature of the cycle. Q_{out} leaves the system only at the lowest temperature of the cycle.]

We would like to eject as little heat as possible, but we have to eject some heat in order to satisfy the entropy conditions as in part (a). Now $dS_{out} = \delta Q_{out}/T_{low}$, where T_{low} is the temperature at which δQ_{out} is ejected. Isolating the output heat, this says $\delta Q_{out} = T_{low} dS_{out}$. From this we can see that in order to have δQ_{out} be as small as possible, we would like T_{low} to be as small as possible as well. Hence we would like to eject <u>all</u> of our heat at the lowest temperature of the cycle. (If we eject heat at higher temperatures instead, we would have to eject more heat in order to keep ΔS_{out} the same.)

We have to eject this heat in order to eliminate the entropy that we introduce during the heat-intake (Q_{in}) portion of the cycle. If the input entropy is as small as possible, then the output entropy and Q_{out} can be as small as possible as well. Hence we would also like ΔS_{in} to be minimized. Since $dS_{in} = \delta Q_{in}/T_{high}$, where T_{high} is the temperature at which δQ_{in} is absorbed, we would like T_{high} to be as large as possible. Hence we would like to take all of the heat in at the highest temperature of the cycle.

Thus we wish to eject all of the heat along an isotherm at T_L, and input all of the heat along an isotherm at T_H. No heat should be input or ejected at any other temperatures. Thus we would like a cycle composed of an isotherm at T_L, and adiabat, and isotherm at T_H, and another adiabat. This is the Carnot cycle.

2. A cyclic heat engine uses an ideal gas as its working substance. Which of the following are true?

___T___   For a complete cycle, the change in entropy of the gas is zero ($\Delta S_{gas} = 0$).

___F___   For a complete cycle, the change in entropy of the gas is zero ($\Delta S_{gas} = 0$), but only if the engine operates reversibly. If the engine operates *irreversibly*, then $\Delta S_{gas} > 0$.

___F___   For a complete cycle, the change in entropy of the universe is zero ($\Delta S_{universe} = \Delta S_{gas} + \Delta S_{environment} = 0$).

___T___   For a complete cycle, the change in entropy of the universe is zero ($\Delta S_{universe} = \Delta S_{gas} + \Delta S_{environment} = 0$), but only if the engine operates reversibly. If the engine operates *irreversibly*, then $\Delta S_{universe} \geq 0$.

Since the gas undergoes a complete cycle, its final state is the same as its initial state. Since entropy is a state function, this means that the final entropy must be the same as the initial state. Hence $\Delta S_{gas} = 0$ for a complete cycle.

This conclusion was independent of how the gas was taken through the cycle. All that matters is that the gas return to the state in which it started. The cycle can be reversible (as in the usual heat engine problems) or irreversible (as in "real" heat engines with friction, or as in cycles with sudden expansions, etc.).

Things are different, however, when we enlarge our system to include the gas plus its environment. (The system might then be called the universe.) Admittedly, the *gas* returns to its initial state at the

end of the cycle, but the *environment* typically does not. (Why should it? By running the engine, we have taken heat from a "hot" part fo the environment and dumped it to a "cool" part of the environment.) So we cannot make the same "state function" argument for the environment that we made for the gas itself.

When an engine operates reversibly, then every bit of heat that flows into or out of the gas, flows out of or into the environment, and at the same temperature. Thus, for every small entropy change dS = dQ/T of the gas, there is an equal and opposite entropy change dS = -dQ/T for the enviroment. So when we consider the universe (= gas + environment), we find a net entropy change of zero.

But when a cycle is irreversible, the entropy changes of the environment are no longer coupled to the entropy changes of the gas in this way. (For an example of this, see Problem 2 below.) So for an irreversible cycle, the entropy change of the universe need not be zero, and in fact is generally positive.

3. A box with total volume V_0 is divided in half by a partition. On the left-hand side of the partition, there is a sample of ideal gas with initial pressure P_0 and initial temperature T_0. On the right-hand side of the partition, the box is empty.

The partition is then suddenly removed, and the gas expands freely to fill the entire box. Soon the gas is in thermal equilibrium again.

a) Intuitively, what do you think happens to the entropy of the gas when it expands freely? Does the entropy increase, decrease, or stay the same? Justify your answer.

Intuitively, we would expect the entropy to have increased. First of all, spontaneous processes in closed systems are often such that $\Delta S > 0$. Also, the final state (with the particles evenly distributed) looks a lot more "likely," or "disordered" than the initial state, which seems rather "ordered" and "unlikely."

b) Suppose that two students, Carolina and Susan, are asked to find the change in the gas's entropy for this process.

- Carolina wants to find the change in entropy as follows:

$$\Delta S = \int_{initial}^{final} \frac{dQ}{T}$$

$$= \int_{initial}^{final} \frac{0}{T} \quad \text{(since no heat flows in or out of the gas during the free expansion)}$$

$$= 0.$$

- Susan, on the other hand, wants to find the change in entropy like so:

$$\Delta S_{\text{ideal gas}} = \tfrac{d}{2} Nk \ln \frac{T_f}{T_i} + Nk \ln \frac{V_f}{V_i}$$

$$= 0 + Nk \ln \frac{V_f}{V_i} \quad \text{(since } T_f = T_i\text{)}$$

$$= Nk \ln 2.$$

Whose method is correct? Why?

Carolina has misapplied the formula dS = dQ/T. This expression only gives the entropy change for a *reversible* process. And since the expanding gas is not in equilibrium the whole time during its free expansion, this process is *irreversible*.

Susan, on the other hand, is correct. To see why, recall that entropy is a state function. That means, once you know the state variables N,p,V,T, you know the entropy. In other words, S is a function of the state variables. And the formula Meghan used is none other than the *explicit* state function S(N,p,V,T).

Notice that since S is a state function, the change in entropy depends only on the endpoints of the transformation. So Susan was perfectly correct to use the above formula, even for this irreversible process.

If Carolina were determined to use the reversible-only formula dS = dQ/T, then she would have to use her imagination. She would have to imagine a series of *reversible* transformations (such as adiabats and isotherms) with the same initial and final points as the free expansion. She could then integrate dS = dQ/T along each of these curves in the p-V plane, and by the end she would find the same answer Susan did. (In fact, she would actually be deriving the formula Susan used!) This process is illustrated in Problem 1 below.

Answers to Problems

1. **a)** Heat flows into the gas.

   b) $\Delta S_{A \to B} = 57.6$ J/K

   c) $\Delta S_{A \to X} = 0$

   d) $\Delta S_{X \to B} = 57.6$ J/K

   e) $\Delta S_{A \to X \to B} = 0 + 57.6$ J/K $= 57.6$ J/K

   f) $\Delta S_{A \to B} = \Delta S_{A \to X \to B}$, since the starting and ending points are the same and *entropy is a state variable.*

   g) $\Delta S_{A \to Y \to B} = 57.6$ J/K

2. **a)** The temperatures don't change because we are dealing with a *free expansion*. See the supplement on free expansions for a detailed explanation of why the temperature remains constant.

   b) $p_B = p_0 / 2$

   c) The net work output is *negative*.

   d) $\Delta S_{A \to B}^{gas} = Nk \ln 2, \quad \Delta S_{B \to C}^{gas} = -\frac{7}{2} Nk \ln 2, \quad \Delta S_{C \to A}^{gas} = \frac{5}{2} Nk \ln 2$

   e) The entropy of the gas adds up to zero, since the gas ends at the same state it started in and *entropy is a state variable.*

   f) $\Delta S_{A \to B}^{environment} = 0, \quad \Delta S_{B \to C}^{environment} = \frac{7}{2} Nk \ln 2, \quad \Delta S_{C \to A}^{environment} = -\frac{5}{2} Nk \ln 2$

g) $\Delta S_{cycle}^{universe} = Nk \ln 2$

3. a) $\Delta S_{H_2O} = -368 \, \frac{kJ}{K}$

b) Since the engine is reversible, the total entropy change of the universe must be 0. Since entropy is a state variable, the entropy change of the engine itself must be zero. Therefore, the entropy change of the cold reservoir must be equal and opposite to the entropy change of the steam/water system: $\Delta S_{cold} = +368 \, \frac{kJ}{K}$. Since the heat is entering the cold reservoir reversibly and at a constant temperature, $\Delta S_{cold} = Q_{out}/T_C$, so $Q_{out} = (273.15 \text{ K}) (368 \text{ kJ/K}) = 1.0 \times 10^5$ kJ. The heat that is input into the engine by the steam condensing into water at its freezing point is $Q_{in} = 1.34 \times 10^5$ kJ, so the first law tells us that the total work output must be: $W_{out} = 3.4 \times 10^4$ kJ.