

## 4.2: Entropy inside and outside- The 2nd Law and the Clausius Inequality

Entropy change is intimately related to heat exchange, which is defined as thermal energy transferred between the system and surroundings. For example, if a system gains  $+\partial q$  of heat from the exterior, then the exterior must have lost  $-\partial q$  of heat. Thus it must be true that both the system and surroundings have also gained / lost entropy, and the sum is the total change of entropy. In fact let's call this the total entropy change of the Universe. This is important because the 2<sup>nd</sup> Law of Thermodynamics states:

**The entropy of the Universe is always increasing.**

Therefore, it is important to calculate the entropy changes in both the system and the surroundings that are exterior to the system. Before we discuss this further, it must be stated that the somewhat simplistic definition  $\partial S = \frac{\partial q_{rev}}{T}$  does not fully describe all the ways that entropy can increase. To illustrate, let's say a system gains  $\frac{\partial q_{rev}}{T}$  amount of entropy from the surroundings. Thus, the surroundings must have lost  $\frac{-\partial q_{rev}}{T}$  worth of entropy. As a result, it appears that the total change in entropy for any heat exchange process is:  $\Delta S_{tot} = \frac{\partial q_{rev}}{T} - \frac{\partial q_{rev}}{T} = 0 \text{ J/K}$ . However, *this isn't necessarily true*; for example, imagine our system is a tin can full of water, and heat is added by the exterior from a candle placed underneath it as in Figure 2.1A. There is an increase the entropy of the system as calculated by  $\frac{\partial q_{rev}}{T}$ . But the setup is very inefficient as a lot of the heat from the candle is not delivered into the system, rather is just wanders off and remains in the exterior. This means that the change in the entropy of the outside is greater than  $\frac{-\partial q_{rev}}{T}$  (meaning it is a less negative number) and thus the sum of the interior and exterior entropy is greater than 0 J/K. You may have figured out already that if we had a perfectly efficient way to input heat from the exterior to the interior, such as that shown in Figure 2.1B, then the total entropy change would in fact be 0 J/K. In the next section will discuss further the differences between inefficient and efficient heating, which is related to reversibility just like we encountered when discussing work in Sec. 2.2.

**4.2.1 Reversible and irreversible heat exchange.** Here we define how an efficient exchange of thermal energy is reversible, whereas a "lossy" (or inefficient) energy exchange is irreversible. To do so we review work from Section 2.2, where we demonstrated graphically how reversible work is always more negative than irreversible. Mathematically this means  $\partial w_{irrev} > \partial w_{rev}$ . To cast a wider net, for any type of work ( $\partial w$ ) we can state  $\partial w \geq \partial w_{rev}$ , as we don't specify whether  $\partial w$  is reversible or irreversible; the equivalence exists in the case of the process being reversible.

Next we consider an isothermal process, which means that  $\partial U = \partial q + \partial w = 0 \text{ J}$  because of the Equipartition theorem. Thus the heat exchanged ( $\partial q$ ) is equal to the negative of work:  $\partial q = -\partial w$ , and as a result anything true for work then the opposite is true of heat. Consequently, if  $\partial w \geq \partial w_{rev}$ , then:

$$\partial q_{rev} \geq \partial q$$

and note that we have not stated whether the heat exchange of the process is reversible or irreversible, and the equivalency is in the event we are describing a reversible heat exchange. If we divide both sides of the above by  $T$ :

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$\partial S \geq \frac{\partial q}{T}$ , we see that:

$$\partial S \geq \frac{\partial q}{T}$$

due to the definition of the change in system entropy as  $\partial S = \frac{\partial q_{rev}}{T}$

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Equation 4.1. If we subtract  $\frac{\partial q}{T}$  from both sides:  $\partial S - \frac{\partial q}{T} \geq 0 \text{ J/K}$

This is the famous Clausius Inequality, and of course the equality holds if the process is reversible.

Here is where we have to discuss interior and exterior changes of entropy further. For the system to experience a heat exchange  $\partial q$  with the exterior, it must be true that the exterior experienced a heat exchange of  $-\partial q$ . As a result, it must also be true that the

change in the exterior entropy is  $\partial S_{\text{exterior}} = \frac{-\partial q}{T}$ . Now let's revise the statement  $\partial S - \frac{\partial q}{T} \geq 0 \text{ J/K}$  as:

$$\partial S + \partial S_{\text{exterior}} \geq 0 \text{ J/K}$$

given that  $\partial S_{\text{total}} = \partial S + \partial S_{\text{exterior}}$  :

$$\partial S_{\text{total}} \geq 0 \text{ J/K} \quad (4.2.1)$$

It seems that we have proven the 2<sup>nd</sup> Law! In fact, we call something “spontaneous” for any process for which the total entropy increases; this is a fancy way of saying that “it happens”. Spontaneous processes include buildings falling down and the cat tearing up the furniture. Likewise, a process that would result in total entropy decreasing could never occur. An example is cooling popcorn back into the form of a kernel. As such, we can understand that the 2<sup>nd</sup> Law means  $\partial S_{\text{total}} \geq 0 \text{ J/K}$ , where the equality sign applies to systems at equilibrium.

To make more progress on our understanding of the 2<sup>nd</sup> Law, let's go back to Equation 4.4:  $\partial S - \frac{\partial q}{T} \geq 0 \text{ J/K}$  and multiply both sides by  $-T$ :

$$\partial q - T\partial S \leq 0 \text{ J}$$

(the greater than / equal sign has been reversed, which occurs because  $-T$  is always negative.) While we wish we could make more of the relationship above, we can't unless we have more information on the thermodynamic process being investigated. For example, we can stipulate that the process is occurring at constant volume. Since the change in internal energy is:  $\partial U = \partial q + \partial w$ , and no work can be done at constant volume, then  $\partial U = \partial q$ . Now we are left with:

$$\partial U - T\partial S \leq 0 \text{ J}$$

and... so what? The above still doesn't mean too much unless we make another stipulation concerning the nature of the process. This time we choose to state that there is no change in the system entropy ( $\partial S = 0 \text{ J/K}$ ). Now:

$$\partial U \leq 0 \text{ J}$$

At this point we can make a “big picture” statement. Recall that the derivation of the above began with:  $\partial S_{\text{total}} \geq 0 \text{ J/K}$ , which again means that the total entropy of a spontaneous process increases. At the end of the derivation we demonstrated that internal energy must decrease or stay the same ( $\partial U \leq 0 \text{ J}$ ). But what does that mean? For example, what happens if internal energy rises? Since we started this derivation with the statement about how a spontaneous process has an increase in total entropy, we ended the derivation *still discussing what makes a process spontaneous*. Which is, for a system under constant volume and constant system entropy, the internal energy must decrease for a process to be spontaneous.

Let's go back to the step in the derivation before we stipulated a constant volume process was at play:  $\partial q - T\partial S \leq 0 \text{ J}$ . What if we were examining a constant pressure system instead? In that case, as we showed in Sec. 3.1:  $\partial H = \partial q$ . Now we have:

$$\partial H - T\partial S \leq 0 \text{ J}$$

and if we stipulate that the process occurs at a constant system entropy:

$$\partial H \leq 0 \text{ J}$$

Now we see that, for a process to be spontaneous under conditions of constant pressure and constant system entropy, the enthalpy must decrease.

To recap, we have accepted the fact that  $\partial S_{\text{total}} \geq 0 \text{ J/K}$  for a process to be spontaneous, which is equivalent to  $\partial U \leq 0 \text{ J}$  under conditions of constant volume and system entropy. However, if the process occurs under constant pressure and system entropy then it must be true that  $\partial H \leq 0 \text{ J}$ . Now do you recall learning in Freshman Chemistry that Gibb's energy must be negative (i.e.  $\partial G \leq 0 \text{ J}$ ) for a process to be spontaneous? Did we just up-end that? We did, and we will explain this discrepancy in the next chapter. Until then there is another facet of entropy that we have to explore concerning the efficiency of car engines and why planes fly at 35 thousand feet.

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