

4.3: Calculating Entropy Changes

While the partial change of entropy is $\left(\frac{\partial S}{\partial T}\right)_V$,

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we must integrate it to measure a finite, quantifiable result:

$$\Delta S = \int \left(\frac{\partial S}{\partial T}\right)_V dT$$

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ΔS

This seems overly easy, especially as we know that nothing is so simple due to the existence of four classes of thermodynamic changes (reversible or irreversible \times adiabatic or isothermal). We might expect a different way of calculating ΔS for each one; however, this isn't the case since S is a state function as described in the following sections.

4.3.1 Changes in System Entropy

Let's start with isothermal, reversible transitions. Isothermal makes T constant, which means that the integral expression above can be simplified by taking the temperature outside of the integral:

$$\Delta S_{isoT,rev} = \int \left(\frac{\partial S}{\partial T}\right)_V dT$$

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$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial q}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial q}{\partial T}\right)_V$$

Recall that, under isothermal conditions $\Delta U = 0$ J, which when coupled with reversibility means $\Delta U = \Delta q_{rev} + \Delta w_{rev} = 0$ J, and thus $\Delta q_{rev} = -\Delta w_{rev} = nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$ according to our learnings in Section 2.2. As a result:

$$\Delta S_{isoT,rev} = \frac{1}{T} \cdot nRT \cdot \ln\left(\frac{V_f}{V_i}\right) = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$$

As for isothermal and irreversible, since ΔS is path-independent the result is the same: $\Delta S_{isoT,irrev} = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. Path independence sure makes our lives easier!

We now move onto to adiabatic transitions. These calculations should be easy because $\partial q_{ad} = 0$ J regardless whether we are doing a reversible or an irreversible transition. And while it appears that there should be no change in the system entropy, in fact this isn't quite true. Recall that we previously stated that the definition of the change in entropy from Equation 4.1: $\left(\frac{\partial S}{\partial T}\right)_V$

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is deficient. To analyze what this really means, let's use the fact that changes in entropy are exact and we can examine adiabatic transitions using two separate steps as shown in Figure 4.2. Under adiabatic conditions both the volume and temperature of the system are affected. As shown in Fig. 4.2 first there is an isothermal change in volume (Path 1), for which we have already determined: $\Delta S_1 = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. In the second step there is a change in temperature under conditions of constant volume. This can only be accomplished through a heat exchange, for which the relevant relationship is: $\partial q = C_V \partial T$ which is true whether the transition is reversible or not. Thus:

$$\Delta S_2 = \int \left(\frac{\partial S}{\partial T}\right)_V dT$$

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$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} \cdot dT$$

The above needs to be converted into a definite integral, the limits of which have the units of the partial (temperature). If we assumed the heat capacity is independent of temperature:

$$\Delta S_2 = C_V \cdot \int_{T_i}^{T_f} \frac{1}{T} \cdot dT = C_V \cdot \ln\left(\frac{T_f}{T_i}\right)$$

Since $\Delta S = \Delta S_1 + \Delta S_2$ as shown in Figure 4.2, the final result is:

$$\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) \quad (4.3.1)$$

Here is some good news- due to the fact that entropy is exact, the equation 4.6 is always “the answer”. It works for every transition; for example, in an isothermal transition the 2^{nd} term is missing ($\ln(1) = 0$), leaving us what we derived in the beginning of this section: $\Delta S_{isoT} = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$.

There are some nuances for calculating ΔS via Equation 4.6 for adiabatic systems. For example, we already stated that it may appear $\Delta S_{ad} = 0 \text{ J/K}$ for all adiabatic transitions because $\partial q_{ad} = 0 \text{ J}$ always. To explore further we will calculate the adiabatic reversible $\Delta S_{ad,rev}$ using the adiabatic equation of state: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ from Equation 2.13, section 2.5.1.1. A small rearrangement yields: $\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}}$, which we can insert into Equation 4.6 for ΔS :

$$\Delta S_{ad,rev} = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left[\left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}}\right]$$

Using the identities $\ln(a^b) = b \cdot \ln(a)$ and $\ln\left(\frac{a}{b}\right) = -\ln\left(\frac{b}{a}\right)$ gives us:

$$\begin{aligned} \Delta S_{ad,rev} &= -nR \cdot \ln\left(\frac{V_i}{V_f}\right) + C_V \cdot \frac{nR}{C_V} \cdot \ln\left(\frac{V_i}{V_f}\right) = \\ &= -nR \cdot \ln\left(\frac{V_i}{V_f}\right) + nR \cdot \ln\left(\frac{V_i}{V_f}\right) = 0 \text{ J/K} \end{aligned}$$

Thus, the system entropy change for adiabatic reversible transitions is 0 J/K . In fact, if you are asked to analyze an adiabatic reversible transition and you correctly apply all the final and initial variables into Equation 4.6 using your calculator, you will find $\Delta S = 0 \text{ J/K}$ although as always be careful with significant figures!

The adiabatic irreversible situation is not so simple. Since the adiabatic reversible equation of state does not apply in the irreversible situation, then it is impossible for the changes in volume and temperature to balance out perfectly. In other words:

$$\Delta S_{ad,irrev.} = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) \neq 0 \text{ J/K}$$

To solve entropy changes for adiabatic irreversible transitions, one has to calculate the change in volume and temperature using $C_V \Delta T = -P_{ext} \Delta V$ as shown in Section 2.5.1.2, and then insert the results into Equation 4.6. If calculated correctly, you will always find that $\Delta S_{ad,irrev} > 0 \text{ J/K}$. As a result, this reveals a small flaw with the expression $\Delta S = \int \frac{dq}{T}$

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$\Delta S = \int \frac{dq}{T}$), which implies that there no changes to system entropy under adiabatic but this is not true. Chemical Engineers have long recognized this issue and resolved it by defining changes in entropy as: $\Delta S = \int \frac{dq_{rev}}{T}$

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$\{T\} + \{\partial S\}_{\text{added}}\}$). The 2nd term is designed to account for the adiabatic irreversible condition, although unfortunately it doesn't help you actually perform any calculations!

4.3.2 Changes in Exterior Entropy

In the previous section we discussed how $\partial S_{\text{total}} \geq 0 \text{ J/K}$ according to the 2nd Law, where the equality is for systems at equilibrium. Here we use this expression to determine how the exterior entropy changes as a function of conditions (isothermal or adiabatic \times reversible or irreversible). We will start with the adiabatic case, which is the easiest to calculate. As adiabatic means there is no heat exchange with the exterior, then it must be true that $\partial S_{\text{ext}} = 0 \text{ J/K}$ regardless of whether the transition is reversible or irreversible. Consequently, adiabatic reversible have a total entropy change of $\partial S_{\text{total}} = \partial S_{\text{ext}} + \partial S = 0 \text{ J/K}$. Likewise, the total change in entropy in the adiabatic irreversible case is $\partial S_{\text{total}} = \partial S > 0 \text{ J/K}$, since the total is equal to the system's change in entropy given the lack of an exterior interaction.

Concerning isothermal transitions, we will start with the reversible which experiences a heat exchange ∂q_{rev} with the exterior. The resultant change in system entropy is $\{\partial S\}_{\text{rev}} = \frac{\partial q_{\text{rev}}}{T}$

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$\{T\}$). Likewise, the exterior experiences a $-\partial q_{\text{rev}}$ with the system and has a change of entropy of $\{\partial S\}_{\text{ext}} = -\frac{\partial q_{\text{rev}}}{T}$

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$\{T\}$). Clearly, $\partial S_{\text{tot}} = \partial S + \partial S_{\text{ext}} = 0 \text{ J/K}$, just like the adiabatic reversible. In fact, the definition of reversibility is $\partial S_{\text{total}} = 0 \text{ J/K}$! To be more specific, recall that we established the formula for isothermal change in system entropy, $\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$, which means that the exterior change is: $\Delta S_{\text{ext}} = -\Delta S = -nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. As for isothermal irreversible:

$$\partial S_{\text{total}} = \partial S_{\text{ext}} + \partial S > 0 \text{ J/K}$$

because $\partial S_{\text{total}} > 0 \text{ J/K}$ is the definition of an irreversible transition. Consequently, some middle-school algebra allows us to determine that: $\partial S_{\text{ext}} > -\partial S$. Integration of this relationship yields: $\Delta S_{\text{ext}} > -nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. This is actually where we stop because we do not have the ability to determine the exact change in ΔS_{ext} ; we can only know that it is greater than the reversible system entropy change. This is because the exterior dynamics may due to some un-knowable action such that the total entropy increases to overcome any decrease in entropy of the system (or didn't decrease enough if the entropy of the system increases). For example, in irreversible heating with a candle as shown in Figure 2.1A, thermal energy is not fully transferred from the exterior (the candle) to the system (the cup of water). This is clearly inefficient and irreversible, and the "lost" energy must increase the exterior entropy more than could ever be discerned from the study of the system alone. Let's take another example, such as a system under compression due to the action of a piston. This lowers the system's entropy. But what actor on the outside of the system is responsible for compressing the piston? If a cat is doing it, then it is guaranteed that the exterior experienced a significant increase in entropy. And the magnitude of the total increase in entropy is unknowable, as any cat owner will tell you.

These results are summarized in Table 4.1. And with this information in our thermodynamics toolkit, we will now determine the theoretical efficiency of gas-burning motor vehicles.

Transition	$\Delta S \text{ (J/K)}$	$\Delta S_{\text{ext}} \text{ (J/K)}$	$\Delta S_{\text{tot}} \text{ (J/K)}$
Isothermal, reversible	$nR \cdot \ln\left(\frac{V_f}{V_i}\right)$	$-\Delta S$	0
Isothermal, irreversible	$nR \cdot \ln\left(\frac{V_f}{V_i}\right)$	$> -\Delta S$	> 0
Adiabatic, reversible	0	0	0
Adiabatic, irreversible	$nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right)$	0	ΔS

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