Module 3

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# Chapter 13. The Second Law

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Summary

Entropy of the system is discovered during the discussions of the four-step reversible cyclic process, isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression of an ideal gas. The cyclic integrals of work, heat and q/T are shown to be zero for this cycle and entropy is defined as dq_{rev}/T which we consider as the second law of thermodynamics as well. General proof for entropy as the state function is provided and the discussions on Clausius led to the recognition of entropy as the property to predict the spontaneity of a given process. Thus, we can predict if a given chemical reaction would occur in a specific reaction, spontaneously, or the reverse reaction is spontaneous or an equilibrium is in control. However, one limitation of entropy as the property to make these predictions is that we need to consider the entropy changes in the system and the surroundings during the change.

Goals

We will recognize the cyclic integrals of work, heat, and dq_{rev}/T for the Carnot cycle and define entropy. General proof that entropy is a state function will be provided by showing the cyclic integral of entropy changes for all cyclic processes is zero. Using this proof, we will examine the Clausius inequality for an irreversible process and recognize the metric that defines the key characteristic of a spontaneous process or a natural process. Using this metric, we will be able to predict if a given chemical reaction would occur or not as well as the direction of the chemical reaction.

13.1 Why Study This?

Entropy is an important thermodynamic function of the system as well as the surroundings. Recognition of entropy as a state function and general proof for this fact is an important milestone in thermodynamics. Entropy plays key role in the thermodynamics of all systems a fundamental mathematical understanding of this key property is critical for applications of thermodynamics. The definition of entropy is considered as the statement of the second law which is vital to our discussions of chemical reactions and physical processes. The tendency of a natural process to occur is fundamentally due to the increase in the net entropy of the system and the surroundings! Therefore, this is a very powerful and important property to identify a spontaneous process or predict if a process will be spontaneous. Entropy changes of a system, during a process, is not a predictor of a spontaneous process. Analyzing the entropy change during a process in the system, however, is very important for our thermodynamic analysis as this will be connected with the enthalpy change in the system. Thus, enthalpy and entropy changes will be our major tools to predict if a given process is natural or spontaneous or not, and thus, the discussion of entropy is a key step in moving forward.

13.2 Reversible Cyclic Process

We begin our discovery of entropy by taking a close look at the work, heat and other changes accompanying a particular reversible cycle with an ideal gas. We use reversible cycles so that we can examine the maximum or the minimum work associated with these steps (state functions) and we use the ideal gas because we precisely know its equation of state. Thus, this cyclic process is also an ideal cycle, and hence, serves as a limiting model to discuss other properties of the system, such as entropy, as we see in the following discussion. We also recognize that the work associated with the isothermal and adiabatic reversible processes are already discussed in the previous sections and hence, we have the corresponding mathematical equations to calculate the W_{cycle} for these processes. First, we simply calculate this term using the four steps shown in Figure 13.1. We will use this cycle to define entropy, and such a definition is also recognized as the mathematical statement of second law of thermodynamics and this statement will be used in deriving a variety of thermodynamic expressions as well as in the discovery of the free energy.
Figure 13.1 An ideal cyclic process consisting of four steps: an isothermal expansion (A to B), adiabatic expansion (B to C), isothermal compression (C to D), and adiabatic compression (D to A) of an ideal gas. The two isothermal processes are carried out at temperatures $T_1$ and $T_2$ where $T_1 > T_2$. This is the Carnot cycle which involves two expansion steps followed by two compression steps, and it is a useful tool to define entropy or the mathematical statement of the second law of thermodynamics. Thus, a very important topic to examine.

The reversible cyclic process that we constructed above the step one converts the initial State A on the left top corner of the diagram (Figure 13.1) via an isothermal expansion at $T_1$ to give rise to state B at the top right corner, at the same temperature. The system is performing work by receiving $q$ from the surroundings, under isothermal conditions. Thus, its internal energy is kept constant during this transformation. Then, during step two an adiabatic expansion converts it to state C at the lower right corner. Because this is adiabatic expansion of the ideal gas, its temperature decreases as it performs work in the surroundings at the expense of its internal energy. This drops its initial temperature from $T_1$ to a lower value $T_2$ at the end of the adiabatic expansion. The temperature decreases in this step because the gas is producing work in the surroundings, adiabatically, at the expense of its internal energy.

Now, the system travels back toward the initial state via the step three, the isothermal compression at temperature $T_2$ from state A to D (bottom left corner), and in the last step (4), the system is converted back to state A via an adiabatic compression which increases its temperature back to $T_1$. The temperature increases in this step because the work is destroyed in the surroundings during the adiabatic process which increases the internal energy of the system raising its temperature. This way, we have A to B as step one, B to C as step two, step C to D as step three, and step D to A as step four. We could have chosen many more steps but that would make it unnecessarily complex and just four steps are sufficient for our discovery of entropy. The system is completely restored to its initial state after the fourth step. We recognize that the entire cycle is reversible where each step is reversible, and hence, the system as well as the surroundings must have been restored to their initial states.

We emphasize that steps one and three are conducted at different temperatures, and that $T_1$ must be greater than $T_2$ and this is because $T_1$ and $T_2$ are connected by the adiabatic reversible expansion, step 2 during which the system is lifting masses in the surroundings at the expense of its internal energy ($\Delta U < 0$). Similarly, step 4 must raise the temperature from $T_2$ to $T_1$ to restore the system to its initial temperature, and this is done by lowering masses in the surroundings during this compression step where the energy is stored as increase in $\Delta U$. Thus, while steps one and three are isothermal with the temperature of the system being unaffected during these processes, steps two and four are adiabatic and the temperature of the system is changing. Whether the temperature is decreasing or increasing during these latter steps depended on if the process is expansion or compression. In all steps, we point out that ideal gas is being used in the system and that all steps are reversible, thus, the whole cycle is reversible. Reversibility of the cycle ensures that there are no permanent changes occurring in the system or the surroundings, and if we run the cycle backwards, the same exact changes will occur. The only difference being that the signs of changes will be reversed. With these descriptions of the individual steps of this unique reversible cycle, we next proceed to write the expressions for $w$, $q$ and $\Delta U$ values for each of these four steps. To do that, we will define the pressures and volumes of the ideal gas at each of the four states, A through D, and observe their changes for each step as well.
13.2.1 The p-V diagram for the Carnot cycle

Using the ideal gas, we construct pressure-volume plots for the isothermal and adiabatic steps (Figure 13.2). We choose pressure on the y axis, volume on the X-axis, and for the reversible isothermal expansion we connect A on the top left with B on the top right where B is lower in pressure higher in volume at temperature $T_1$. Next, the expansion continues with increase in volume and drop in pressure during the adiabatic step. The adiabatic expansion involves decrease in temperature with a steep drop in pressure, as the volume increases and reaches state C. This completes the first half of the cycle.

![Figure 13.2 Pressure-volume plot for Carnot cycle](image)

Figure 13.2 Pressure-volume plot for Carnot cycle, where the step one is the expansion with increase in volume and decrease in pressure. The second step continues the expansion further under adiabatic reversible process with steeper decrease in pressure and increase in volume converting state B with state C. The steeper drop in pressure is due drop in temperature during the adiabatic expansion. The steps three and four follow the same exact steps in the reverse through states D back to A. Note that these steps run parallel to the first two steps.

The journey back involves the isothermal compression with a decrease in volume but increase in pressure from point C to D. We recognize that this is Boyle’s law isotherm of reversible compression and this is parallel to step one but at temperature $T_2$. The step four is the adiabatic compression which runs parallel to the step two, connecting D with A. Again, the steep increase in pressure is due to adiabatic compression where the temperature increases from $T_2$ to $T_1$. Thus, the pressure-volume plot forms a parallelogram where each step is curved. To further identify the four states, we assign pressures $p_1$ thorough $p_4$ and volume $V_1$ through $V_4$ for the four steps, as shown in Figure 13.2. Therefore, we have started from initial values of $p_1$, $V_1$ and returned the back to this original state, and therefore this is the p-V diagram of the cyclic transformation.

13.2.2 The $w$, $q$ and $\Delta U$ terms for the Carnot cycle

We already announced that the temperature of the isothermal step one is $T_1$ and that of the step three is $T_2$ but $T_1 > T_2$ and this is because the adiabatic expansion in step two lowers the temperature of the system. Since these are isothermal steps, $\Delta U$ with either of the two steps are equal to zero, as shown in Figure 13.3. Thus, applying the first law, we deduce that the $q$ values for steps one and three are as $q_1 = w_1$ and $q_3 = w_3$. We will look at this cyclic process and write the $w$, $q$, and $\Delta U$ terms for all the four steps, and then figure out $W_{cycle}$ (Table 1).
The adiabatic steps three and four are connected through their respective temperatures and volumes. We can simplify this relation even further by connecting the volume changes using the adiabatic relation. Between the same temperatures and cancel, each other out. The remaining terms are the sum of which are exactly equal but opposite in direction. These are adiabatic reversible processes occurring cyclic work is written in a more compact form, after cancelling the work terms for the steps two and four, taking \(-nR\) as common, we get the following expression. Writing the values of work for these steps from Table 1, we write the following expression, where the terms for each of the four steps are summed together.

For the second step, the adiabatic expansion, we recognize \(q\) is zero, and hence, work is equal to \(\Delta U\). Since this is reversible adiabatic expansion temperature decreasing and \(\Delta U\) is given as \(C_v(T_2-T_1)\) which is also equal to \(w_2\).

Now, we recognize the second half of the cycle, with isothermal reversible compression in step three, which is similar to step one but the volume is decreasing. So, the work \(w_3\) is given as \(-nRT_2 \ln(V_4/V_3)\). As this is isothermal, \(\Delta U\) is zero and \(q\) is equal to \(-w_3\). The last and the final step is the adiabatic compression with \(q\) as zero and \(w_4\) equal to \(\Delta U\), which is given as \(C_v(T_1-T_2)\), where \(T_1\) is the final temperature and the system is restored to its initial state.

So, this kind of an analysis for each of these steps is important and we need to clearly understand what is the basis for writing the terms of each of these steps. Now we can calculate the \(w\), \(q\) and \(\Delta U\) for the entire cycle, as following.

### 13.2.3 Work done in one cycle

As the system passes through the cycle, we can argue that \(W_{cycle}\) and \(q_{cycle}\) will be simply the sum of the corresponding values of the individual steps. For example, \(W_{cycle}\) is given as following, where the work terms for each of the four steps are summed together.

\[
W_{cycle} = w_1 + w_2 + w_3 + w_4
\]

Writing the values of work for these steps from Table 1, we write the following expression, where the cyclic work is written in a more compact form, after cancelling the work terms for the steps two and four, which are exactly equal but opposite in direction. These are adiabatic reversible processes occurring between the same temperatures and cancel, each other out. The remaining terms are the sum of the work for the first and the third steps, and taking \(-nR\) as common, we get the following expression.

\[
W_{cycle} = -nR \left[ T_1 \ln(V_2/V_1) + T_2 \ln(V_4/V_3) \right] = -nR \left[ T_1 \ln(V_2/V_1) + T_2 \ln(V_4/V_3) \right]
\]

We can simplify this relation even further by connecting the volume changes using the adiabatic relation. The adiabatic steps three and four are connected through their respective temperatures and volumes, from the previous chapter, \(\gamma\) is the ratio \(C_p/C_v\), as following.

\[
T_1 (V_2)^{\gamma-1} = T_2 (V_3)^{\gamma-1}
\]

\[
T_1 (V_1)^{\gamma-1} = T_2 (V_4)^{\gamma-1}
\]
By dividing the first equation by the second, we release the temperature terms and get the relation between the volumes as following.

\[
\frac{V_2}{V_1} = \frac{V_3}{V_4}
\]

Using this relation, we write \( W_{cycle} \) from the above equation in a simpler form, as below.

\[
W_{cycle} = -nR\left[ T_1\ln\left(\frac{V_2}{V_1}\right) - T_2\ln\left(\frac{V_2}{V_1}\right) \right]
\]

\[
W_{cycle} = -nR\ln\left(\frac{V_2}{V_1}\right)(T_1 - T_2)
\]

We recognize that the equation for the cyclic work is now depends on the temperature differences between the two isothermal steps and the volume changes. Therefore, we can write three particular angles for the discussion of the physical meaning and mathematical consequences of this equation for work.

**13.2.3.1 Case 1: \( W_{cycle} \) when \( T_1 = T_2 \)**

The general expression for the \( W_{cycle} \) obtained for the Carnot cycle reduced to an interesting limit when the temperatures of the step on and step three are identical.

\[
W_{rev, cycle} = 0, \quad T_1 = T_2
\]

Figure 13.4 Pressure-volume plot for Carnot cycle under three specific conditions. Case 1 (left): when \( T_1 = T_2 \). The parallelogram turns into a line with zero area enclosed (\( W_{cycle} > 0 \)) and the adiabatic steps collapse to points. Case 2 (middle): when \( T_1 > T_2 \) and \( V_1 < V_2 \), the parallelogram has a finite area, and \( W_{cycle} < 0 \) or masses are raised in the surroundings. Case 3 (right): when \( T_1 < T_2 \), the parallelogram still encloses a finite area (\( W_{cycle} > 0 \)) and the net amount of work destroyed in the surroundings.

That is, the two isothermal steps are occurring at the same temperature and hence, our parallelogram becomes a single line, with no area enclosed (Figure 13.4). This is because the \( W_{cycle} \) equals to zero, when \( T_1 = T_2 \), from the above equation. Therefore, steps two and four don’t exist. Thus, one of the limiting values of the work for this kind of a cycle is that as the temperatures of the isothermal steps approach each other, the cyclic work approaches zero.

**Case 1:** \( W_{cycle} = -nR\ln\left(\frac{V_2}{V_1}\right)(T_1 - T_2) = 0 \)

We also recognize that the graph collapses to a line because the cycle is reversible and if the cycle were not reversible, this can’t happen. Moving forward, we ask how do we maximize the work derived from this cycle, which leads to the second case, discussed below.

**13.2.3.2 Case 2: When \( T_1 > T_2 \) and \( V_1 < V_2 \)**

When the cycle runs at two separate temperatures as in the case of your automobile engine, and when there is expansion (\( V_1 < V_2 \)) then, both terms in the above equation are positive. Your automobile engine is a cyclic engine but not reversible engine and hence, these arguments are applied only qualitatively at this time. We can construct an imaginary automobile engine that runs this reversible cycle and these arguments apply quantitatively for such engines.

**Case 2:** \( W_{cycle} = -nR\ln\left(\frac{V_2}{V_1}\right)(T_1 - T_2) < 0 \)
We note that work is negative, nevertheless, which indicates that a net amount of work is produced in the surroundings or the masses are raised or our automobile moves forward. Then, the area enclosed by the parallelogram is non-zero (Figure 13.3, middle) and it can be measured by simple geometry. Larger the value of $\Delta T$, greater the work produced in the surroundings, and modern automobile engines work at higher and higher temperatures, producing more and more work from the same amount of fuel burned. But, this requires special oils to cool the hotter and hotter engines, which is an entirely different problem to deal with. Viewing from a different angle, when $T_1 > T_2$, the expansion is taking place at a higher temperature than the compression, producing more work during the expansion but consuming less work during the compression to prepare the system for the next cycle. This is how all heat engines such as the automotive or steam engines work, which are not reversible cyclic engines.

13.2.3.3 Case 3: When $T_1 < T_2$ and $V_1 < V_2$

The last possibility we consider is the case when the expansion occurs at a lower temperature than the compression. Examining the above equation for work, we see that $\Delta T < 0$, $\Delta V > 0$ and the work term will also be $>0$ or a net amount of work is destroyed in the surroundings. Mases will be lowered in the surroundings, at the end of each cycle. This appears to be a wasteful process, but such a cyclic irreversible process is used in refrigeration and hence, highly relevant, later. The p-V diagram for the original reversible process will still enclose a finite area, but the sign of the work will be positive (Figure 13.4, right). The above three separate cases provide how the work term changes, based on the experimental conditions, in a drastic manner.

$$Case\;3:\;W_{cycle} = -n\;R\;\ln\left(\frac{V_2}{V_1}\right)(T_1 - T_2) > 0$$

As mentioned earlier, these cases provide additional insight into the nature of this famous cycle which we will use to define entropy, shortly. Before that, we will examine the $q$ terms for each of the four steps.

13.2.4 $Q_{cycle}$

We now write $Q_{cycle}$ just as we wrote $W_{cycle}$ and $q_{cycle}$ is the algebraic sum of the $q$ values for the individual steps of the cycle, as following, where $q_1$ is for step one, it is zero is for the adiabatic step two, $q_2$ is for the step 3 and $q$ for this adiabatic step is also zero. In addition, we recognize that $\Delta U = 0$ for any cyclic process and hence, heat and work terms are related by the first law of thermodynamics. Thus, we get the following expression for the heat terms of the Carnot cycle and relate to the $W_{cycle}$.

$$q_{cycle} = q_1 + 0 + q_2 + 0 = -W_{cycle}$$

$$q_{cycle} = -W_{cycle} = n\;R\;\ln\left(\frac{V_2}{V_1}\right)(T_1 - T_2)$$

The values of the heat terms for each of the four steps are given in Table 1, and we have discussed these values in sufficient detail. In each case, we apply first law of thermodynamics to obtain the $q$ value, unless it is an adiabatic process where the corresponding $q$ is zero.

One other detail we need to examine is the energy and enthalpy terms of this cyclic process which are zero, because these are state functions. Thus, we obtain two additional relations for the Carnot cycle.

$$\Delta U_{cycle} = 0$$

$$\Delta H_{cycle} = 0$$

13.3 Discovery of Entropy

Just as above, we will examine the quantity $q/T$ for this particular cycle. We will see that this exercise leads to the discovery of entropy. So, let's sum "$q/T$" for the cycle and see what we get. That is, we will sum the "$q/T$" terms for the four steps and this is pretty straight forward as we already have the values of $q$ for each of the steps. Using Table 1, we write the following steps.

$$(q/T)_{rev.\;cycle} = (q_1/T_1) + 0 + (q_2/T_2) + 0$$

$$= -\left(\frac{w_1}{T_1}\right) - \left(\frac{w_2}{T_2}\right)$$
In the penultimate step, we have the relation for the adiabatic transformations connecting the four volume terms, and use the relation $V_1/V_2$ is exactly equal to $V_4/V_3$. Thus, the volume terms cancel to give zero for this entire sum. Thus, we can define a new state function as follows.

$$dS = \frac{dq_{\text{reversible}}}{T}$$

The new state function is obtained because this cyclic integral is zero, where the $q$ is for a reversible cycle. Since, $q_{\text{reversible}}$ is a state function, dividing it with temperature should also provide a state function but we will examine this quantity in sufficient depth and show that this new quantity, entropy ($S$) is a state function.

In summary, when considering a reversible cycle, we recognized a new state function called entropy, given as $q_{\text{reversible}}/T$.

### 13.3.1 The statement of the second law of thermodynamics

From the above discussions, we can simply state that the definition of entropy itself is considered as the second law of thermodynamics and it is the starting point to derive a large number of thermodynamic functions, thus a foundation stone of thermodynamics.

$$dS = dq_{\text{rev}}/T$$

The second law states that a cyclic engine working with a single heat reservoir can’t produce a net amount of work in the surroundings or the $W_{\text{cycle}}$ is $\leq 0$, for any cycle operating with a single heat reservoir.

$$\int_{\text{cycle}} \frac{dQ}{T} > 0$$

We can dwell into this aspect of the second law by recalling that when the two temperatures are equal for the Carnot cycle, single heat reservoir, then $W_{\text{cycle}}$ is zero (Figure 13.5, left). However, we have to point out that Carnot cycle is a reversible cycle and we can say that for all reversible cycles, this must be true. Let’s consider that we have a piston and a cylinder with a certain amount of gas, at a pressure greater than room pressure, in equilibrium with a thermal bath kept at room temperature.

During the forward process, we allow it to expand reversibly, raising masses in the surroundings. In the reverse process, we compress it back to its initial state by lowering certain masses in the surroundings, reversibly. The work terms are exactly equal in the two processes but opposite in sign, and the net amount of work derived during the cyclic process is zero. This will be the case for all reversible cycles because the steps are reversible. This is one part of the proof.
Figure 13.5 The work produced or consumed during a cyclic process. (Left) Reversible cycle with the system in equilibrium from left to right and during the reverse process, the system moves back from final state to the initial state. (Right) Irreversible, one step expansion where the work produced is given by the small blue rectangle, followed by single step compression where the work needed to traverse back is much greater (larger purple rectangle).

The other part follows, when we consider irreversible cycles. The gas will be expanding irreversibly during the first step (Figure 13.5, right), and the system is raising masses in the surroundings. The blue rectangle is the area (W) under the p-V curve, and the sign of work is negative. In the reverse process, we compress the gas to its initial state but now this takes much more amount of work or larger masses are to be lowered to compress the gas to its initial state (purple rectangle) than produced during the expansion process. We have already calculated these work terms in the previous chapter. Thus, for the irreversible cycle, a net amount of work is destroyed in the surroundings (\( W_{\text{cycle}} < 0 \)), and no net amount of work is gained from the system. From the above two discussions, we can conclude the following.

\[
W_{\text{cycle}} \leq 0 \quad \text{(the second law of thermodynamics)}
\]

We immediately recognize, that if you have two or more different temperature heat reservoirs then, you will be able to extract certain amount of work from the system. This aspect is described below, in detail.

13.3.2 The second law and the efficiency of heat to work conversion

Every form of energy can be converted into heat completely. But conversion of heat into other forms of energy is thermodynamically limited. For example, you have electrical current passing through a coil producing heat. You can produce almost exactly the amount of heat that is equal to the total electrical energy consumed or that the efficiency is 100%. If we take certain mechanical energy and convert into heat, we can do what is called the mechanical equivalent of heat, with 100% efficiency. Light also can be converted into heat with 100% efficiency, and we can completely convert all other forms of energy into heat. This leads to yet another statement of the second law.

The conversion of heat to other forms of energy is problematic and this is where the second law of thermodynamics sets limits on the efficiency of such conversion, for example. The efficiency of converting heat to work by a cyclic engine, operating between two heat reservoirs, is given as the net amount of work done in the surroundings divided by the heat absorbed during the expansion step. Recall the Carnot cycle and the notations for each of the four steps (Figure 13.6). Recall the expression for the \( W_{\text{cycle}} \).

\[
\varepsilon = \frac{W_{\text{cycle}}}{q_1}
\]
Figure 13.6 The four states, A, B, C, and D of the Carnot cycle are connected by processes 1, 2, 3, and 4 of the cycle. The red horizontal curves represent isothermal steps at temperatures $T_{\text{high}}$ and $T_{\text{low}}$, while the steep blue curves represent the adiabatic steps. The cyclic work is given by the area enclosed by these four curves.

We note that $q_1$ is the heat supplied during the isothermal expansion at the high temperature during the isothermal process and only part of this is used to produce work. The efficiency is the ratio of the work produced and all the heat supplied to do the expansion work. After substituting the expression for work and $q_1$, in the above equation, we see that we can cancel $n$, $R$, $\ln(V_2/V_1)$ and get a more compact expression, as follows.

$$
\epsilon = (n R \ln(V_2/V_1)) \left[ T_{\text{high}} - T_{\text{low}} \right] / (n R T_{\text{high}} \ln(V_2/V_1))
$$

$$
= \left[ T_{\text{high}} - T_{\text{low}} \right] / T_{\text{high}}
$$

$$
= 1 - (T_{\text{low}}/T_{\text{high}})
$$

$$
\leq 1
$$

We recognize that $T_{\text{high}}$ and $T_{\text{low}}$ are the initial and final temperatures of the step 2, an adiabatic expansion process for an ideal gas. When an adiabatic expansion occurs, the temperature of the system drops. Therefore, $T_{\text{low}} < T_{\text{high}}$. Since we are subtracting this ratio from 1, the efficiency has to be less than one with a maximum value of 1. Two limiting cases are immediately deduced from these arguments. The efficiency approaches 1 as $T_{\text{high}}$ approaches infinity or $T_{\text{low}}$ approaches 0, and sets one as the maximum efficiency to be achieved. Thus, the second law clearly states that the efficiency can never be greater than 1. This is also consistent with the first law, because you could not produce more work than the heat drawn from the surroundings. These are important consequences of the second law.

The other limit imposed by the second law is that the efficiency equals zero when $T_{\text{low}}$ equals $T_{\text{high}}$. In this case, the heat engine operates at one temperature, or at a single heat reservoir and its efficiency is zero or it can’t produce work. This is the other statement of the second law we discussed.

Indeed, Carnot engine is an ideal engine, it is the best you can hope for. A real engine, on the other hand, is very likely to have efficiency less than the ideal engine. The larger the value of $T_{\text{high}}$, the greater will be the efficiency, and the higher the better. Similarly, lower the value of $T_{\text{low}}$, greater the efficiency, lower the better. Thus, the second law predicts that larger the difference between the two temperature reservoirs, greater would be the efficiency of the engine and maximum efficiency is obtained when the highest temperature reaches infinity or the lowest temperature reaches 0 K. These provide limiting conditions for the efficiencies.

Another manifestation of second law of thermodynamics is given in terms of the efficiency in terms of $q_1$ and $q_2$. It is defined as 1 plus the ratio of $q_2$ given up at low temperature during the compression to $q_1$ gained at high temperature during the compression. Thus, we cast as the following where we replace $q$ terms with the corresponding $T$ terms, as they are proportional.

$$
\epsilon = \frac{W_{\text{cycle}}}{q_1}
$$
One of the reasons the modern gas engines are becoming smaller and smaller is that they run at higher and higher temperatures to extract more and more work from the burning fuel. Therefore, they require engine oils that can withstand these higher and higher temperatures. The second law, therefore, is another example of practical, down to the earth, real life importance.

### 13.3.3 Thermodynamic scale of temperature

The second law also sets a limit to the lowest temperature that can be achieved in the universe. If $T_{\text{low}}$ approaches zero, then the efficiency approaches 1 but low temperature can’t go negative because this raises the efficiency above 1. That is no engine can have efficiency above 100% (violation of the first law) and hence, 0 K is the absolute lower limit to be achieved.

![Figure 13.7 Plot of efficiency of the Carnot engine on the Y-axis as a function of the $T_{\text{low}}$ on the X-axis for a fixed $T_{\text{high}}$. The equation for efficiency shows that the intercept has to be one and the slope negative. As the low temperature approaches zero, efficiency approaches 1. The temperature can’t be negative because that will force the efficiency to go above one which is not possible, as explained above. This is also considered as the Second Law of Thermodynamics.](image)

This situation is illustrated in Figure 13.7 where the efficiency is plotted as a function of $T_{\text{low}}$ for a fixed $T_{\text{high}}$. The equation for efficiency shows that the intercept has to be one and the slope negative. As the low temperature approaches zero, efficiency approaches 1. The temperature can’t be negative because that will force the efficiency to go above one which is not possible, as explained above. This is also considered as the Second Law of Thermodynamics.

No part of the universe can have temperature less than zero, if it does then the Carnot engine can have efficiency greater than 1, but this against the first law. This defines the absolute zero kelvin and a totally new insight into temperature has been realized. Therefore, the Kelvin scale of temperature is also as the thermodynamic scale of temperature. Of course, even obtaining zero K is impossible and so far, we are only able achieve few hundred µK.

### 13.3.4 Graphical illustrations of the Carnot Cycle

To summarize the relation between the Carnot cycle and specific thermodynamic variables, we plot a few different ways (Figure 13.8). The plot on the right top illustrates how the $U$ versus $V$ plot looks like. The states 1 and 3 are shown and the two isothermal processes are shown by the arrows indicating the directions of the path.

![Plot of $U$ vs $V$](image) ![Plot of $T$ vs $S$](image)
Figure 13.8 Plots of a few thermodynamic function for the Carnot cycle. The right top shows how U and V vary during the cycle forming a parallelogram, and left top indicates how the T and S vary during the cycle progresses as a rectangle. The states 1 and 3 at the opposite corners and such plots are also indicated for T vs q (bottom left) and q vs w (bottom right).

During the isothermal expansion process from state 1, the U is constant but V is increasing linearly and hence, it is a line parallel to the X-axis. During the adiabatic expansion, U is decreasing linearly with further increase in V to reach state 3. Thus, the plot is a parallelogram completed by the reverse steps back to state 1.

Thus, one can plot in many different ways but recognizing how the variables change during the specific processes of the Carnot cycle. For example, T vs S is a rectangle (Figure 13.8, top right), just as T vs q (Figure 13.8, bottom right) while q vs w is another parallelogram (Figure 13.8, bottom right). These plots give us a more comprehensive understanding of Carnot cycle, and cements our recognition as well as the familiarity with Carnot cycle.

you examine the plots in the previous slide plot H versus P and H versus Q

13.4 Molecular interpretation and applications in daily life

Molecular interpretation

The second law of thermodynamic is a law of practical observations and does not require a molecular basis. However, it should be understandable from molecular principles as well. Since energy can neither be created nor destroyed, the first law states that it is to be conserved in all processes. We may simply convert one form of energy to another but not create it and the first law does not state if it is possible to convert heat to work, for example, but we know that all forms of energy can be converted into heat. However, the heat is a manifestation of the random motion of the molecules and if we want to convert this into directed-motion or work, then certain conditions might apply. Because we need to impose certain degree of order on the disordered motion and so, the entropy of the particles need to be reduced to perform work. The second law governs this concept and states conditions under which heat can be converted into work and puts limits on the efficiency of work that can be produced from heat. Therefore, entropy and the second law are intrinsically connected at the fundamental level. Entropy and heat are connected at the molecular level as will be described in the next chapter. Heat can’t be converted
completely to work because some degree of disorder is introduced even in the process of producing work, increased volume under isothermal conditions increases entropy. Only the adiabatic work production does not increase or decrease entropy because q is zero. Thus, we can’t reduce entropy by performing work but certain degree of order is required to produce work. This interpretation is still can’t explain the limits placed by the second law but provides some insight into the connections at the fundamental level.

Applications in daily Life

The thermodynamic laws are foundation stones for our discussions of thermodynamics and their applications in real life as well as practical applications or fundamental arguments. The second law, for example, governs the efficiencies of all heat engines and influences the design of planes, trains and automobiles or any devices where heat engines are used. Thus, both in the lab and in life, entropy and the second law are of extreme importance.

Although the application of the second law to chemical reactions is limited the application of the concept of entropy is extensively examined in this book. Entropy also plays a vital role in real life and entropically driven chemical reactions and physical process are abundant. Simple expansion of a pressurized gas is driven by increase in entropy. The mixing of sugar cubes in your coffee, in the morning or evening, is driven by entropy, as well as the expansion of the universe. Thus, net entropy of the universe is increasing and hence, the saying that ‘entropy is not what it used to be’. There will be numerous examples of entropy in the remaining chapters as well.

13.4.1 Units and worked out examples

Units

Work has the units of energy, ergs, joules, calories etc., and efficiency is dimensionless quantity.

Worked out example

1. Define the path, surroundings, system, work and efficiency when the hot gases expand during the combustion of the internal combustion engine of the car. Use your imagination to choose appropriately.

We define the cylinder with fuel filled before the spark plug ignites and the boundary of the gas separating the surroundings from the system. We choose this as an open system so that we can add the fuel, spark the plug and allow the work to appear at the boundary of the system as the piston moves to expand the gases. We heat the gases by igniting and burning the fuel with oxygen in the cylinder and transfer some energy to the surroundings. As the hot gases expand almost instantly, we can consider this as adiabatic expansion and the temperature of the gas should drop. As the piston is moved up during this step, the masses are raised or the crank shaft turns producing power to move the car. After this step, the burnt gases are released in the environment (thus, polluting the air around) and mass is being moved out of the system and into the surroundings. Thus, the open system is the correct choice for this example. The path is clearly expansion followed by compression, getting ready for the next stroke.

2. Calculate the work done when a gas expands in an automobile engine from an initial volume of 200 cc to a final volume of 500 cc, against a constant external pressure of 2 atm, adiabatically.

Work done = - \( p_{\text{ext}} \cdot (V_{\text{final}} - V_{\text{initial}}) = - 2 \text{ atm} \times 300 \text{ cc} \ (1 \text{ L/1000 cc}) = - 0.6 \text{ atm L} \)

13.4.2 Key points and terms

Key points

1. The definitions of Carnot cycle, entropy, and the second law are fundamental for the discussions of thermodynamics of our chemical systems.

2. Carnot cycle is a reversible cycle of expansion and compression involving four distinct steps and four distinct states. The work and heat terms of each of the steps are obtained simply applying the first law or the definitions of pV work.

3. During the cycles such as Carnot, we showed that the \( (q_{\text{reversible}}/T)_{\text{cycle}} = \Delta S = 0 \).

4. Thus, discussion of the Carnot cycle led us to discover a new state property, entropy.
5. If we show that above relation in item 3 is true for any cycle, then we have the final proof that entropy is a state function. This will be done in the next chapter.

6. The second law puts certain limits on our attempts to convert heat to work. The maximum efficiency for this conversion can occur only when the high temperature reaches infinity or the low temperature reaches 0 K.

7. At all other temperatures, the efficiency that can be achieved is precisely predicted by the second law and thus, it is of high practical importance.

8. The second law also puts an absolute limit to the lowest temperature in the universe as 0 K.

9. Thus, the thermodynamic scale of temperature is established firmly based on experimental measurements and this is also the kelvin scale of temperature.

**Key terms**
Cyclic work, reversible cycle, Carnot cycle, efficiency of a heat engine, entropy, definition of entropy, the second law in various manifestations, and finally the lowest temperature that can be attained as well as the thermodynamic scale of temperature.

**13.4.3 Graphing Assignment**
Plot H vs U, H vs T, H vs p and H vs q for the Carnot cycle.

**13.5 Further Reading**
https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-8-second-law/

**13.6 Self Tests**

**13.7 Self Tests Key**
# Chapter 14. Entropy and its Properties

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Summary
General proof for entropy as a state function is worked out in detail and entropy is firmly established as a state function, for any given process. The dependence of entropy on pressure, volume, and temperature has been established which is useful for analyzing if a given process occurs spontaneously or not. These dependencies are used to define the standard entropy of an ideal gas and expressions for entropy with these variables are derived. Next, the third law of thermodynamics was stated, and its use for calculating the absolute entropies of substances at room temperature and 1 atm has been delineated in sufficient detail.

Goals
We will work out the general proof for entropy as a state function and then examine its dependence on V, T, and p. We will investigate the standard entropy of ideal gas and examine its dependence on p, V, and T as well. Using the dependence of entropy on pressure and temperature and with third law of thermodynamics, we will construct a path to calculate the entropies of substances. This will be an achievement because it provides an experimental method to obtain the entropies of substances at any pressure and temperature. Finally, we will examine molecular descriptions of these phenomenon.

14.1 Why Study This?
Entropy is a key thermodynamic variable and establishing that it is a state function is important for all our discussions of spontaneous processes and other aspects of thermodynamics. This is will be accomplished in the first of this chapter. We will be examining if entropy can predict the spontaneity of process or predict the direction of a process, successfully. Thus, entropy is an important property to recognize. Equally important is to establish how entropy depends on the three major thermodynamic variables, p, V, and T. Then, we can examine if a given process can become spontaneous under a specific set of p, V, and T or how to vary these such that a given process can become spontaneous. In our daily lives, we encounter numerous spontaneous processes and controlling their direction is an important technological achievement necessary for our culture to thrive. Thus, any insight gained at the molecular level to control these processes is vital. For example, chemists want the reactions to occur upon mixing the reactants under specific set of p, V, T, and concentration or other conditions. These conditions should be such that the reaction occurs spontaneously so that products can be obtained. Thus, predicting under what conditions will a chemical reaction or a physical process happens is of significance. Since entropy is a key player here, we need to figure out what it is and what its properties are. Thus, this chapter is important to make progress toward our quest of understanding the answer to the enquiry, why do chemical reactions occur?

14.2 General Proof for Entropy is a State Function
We will show that the cyclic integral dS is 0 for any cyclic process, not just for the Carnot cycle or any reversible cycle. This proof is provided in two separate parts. Our strategy is to construct any cyclic process and evaluate the cyclic integral \( \frac{dQ_{\text{rev}}}{T} \) to test if it is equal zero. We will assume that for any given cycle "\( \frac{dQ}{T} \)" is greater than zero, and if that results in an impossible consequence, then we know it must be wrong. Then, we will assume that the cyclic integral is less than zero, and if this also results in an impossible consequence, then we know for sure that the cyclic integral for any cycle must be zero. With this strategy, we move forward. This is the scientific approach, you assume and then test if that assumption is correct or not before acting on it.

We need to prove that for all cycles, reversible or not, the cyclic integral of dS must be zero, and from the definition of entropy, we need to show the following integral vanishes.

\[
\int_{\text{cycle}} \frac{dQ_{\text{rev}}}{T} = 0
\]

We assume that this integral is greater than zero, as below, for any cycle.

\[
\int_{\text{cycle}} \frac{dQ}{T} > 0
\]
We have any cycle of choice (cycle 1) and let it be coupled with the Carnot cycle, the cycle that we are familiar with. It is ok to couple different cycles because it generates a new cycle which also qualifies as a cycle.

![Composite cycle constructed from any cyclic process (cycle 1) and couple it with the Carnot cycle to generate a composite cycle. This cycle is also not a reversible cycle, even though the Carnot cycle is a reversible cycle. Thus, this cycle is also like any cycle we chose before. Thus, for this composite cycle, we can write the following, from the assumption we made.](image)

From our assumption above, we can now write the following for the composite cycle as well, where \(dQ_{\text{composite}}\) is the corresponding heat term for the composite cycle.

\[
\int_{\text{cycle}} \frac{dQ_{\text{composite}}}{T} > 0
\]

We can justify this further. Because the composite cycle has two different cycles embedded in it, we can write this as a sum of two separate terms, where the first term in the integral is from cycle 1 we chose initially, and the second term is for the Carnot cycle. But we know from the previous chapter that the corresponding cyclic integral for the Carnot cycle is zero. Therefore, simply adding a zero to the cyclic integral of any cycle we chose, should not make it equal to or less than zero.

\[
\int_{\text{cycle}} \frac{dQ}{T} + \int_{\text{cycle}} \frac{dQ_{\text{carnot}}}{T} > 0
\]

\[
\int_{\text{cycle}} \frac{dQ_{\text{carnot}}}{T} = 0
\]

The corresponding work terms for the composite cycle (\(W_{\text{composite}}\)) in terms of the work of cycle 1 (\(W_{\text{cycle}}\)) and that of Carnot cycle (\(W_{\text{carnot}}\)).

\[
W_{\text{composite}} = W_{\text{cycle}} + W_{\text{carnot}}
\]

Now, we adjust the work produced by the Carnot cycle such that its direction and the magnitude be opposite to that of the cycle 1, then this results in no net amount of work for the composite cycle. This should be readily feasible from the discussions of the previous chapter where we learned to adjust the work term for the Carnot cycle. For example, we can adjust the temperatures of the isothermal processes or by controlling the volume or pressure changes of the Carnot cycle, we can control the area enclosed by the Carnot cycle and hence control the magnitude of work (Figure 14.2). We can run the Carnot cycle forward or in the reverse direction, as needed, to make the work of the composite cycle zero.

\[
W_{\text{composite}} = 0
\]

![Illustration of Carnot cycles producing different amounts of work.](image)
Using the first law, we can write the following relation and write the work in terms of heat, using the first law of thermodynamics and \( \Delta U = 0 \) for any cycle.

\[
W_{\text{composite}} = - Q_{\text{composite}} \quad \text{as} \quad \Delta U = 0
\]

Now, we can write \( Q_{\text{composite}} \) in terms of individual \( Q' \) terms of the individual steps of the composite cycle \( Q_1, Q_2, Q_3, Q_4, \ldots \) for steps 1, 2, 3, 4, etc., as following, which must also be equal to zero. This is one of the conditions we will use, shortly.

\[
Q_{\text{composite}} = Q_1 + Q_2 + Q_3 + \ldots = 0
\]

We have just shown for the composite cycle, the following is true.

\[
\int_c \frac{dQ_{\text{composite}}}{T} > 0
\]

Now, writing individual terms of integral of the composite cycle with temperatures \( T_1 \) for step 1, \( T_2 \) for step 2, \( T_3 \) for step 3, etc., we can write the second condition as following.

\[
\int_c \frac{dQ_{\text{composite}}}{T} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \ldots > 0
\]

Under what conditions both these two equations are mathematically valid? We take a closer look at these two conditions, one at a time.

**14.2.1 Condition 1**

Here, we examine all the heats of the composite cycle, and their sum is zero. Some will be exothermic, some will be endothermic and some may be adiabatic. Whatever it may be, the Carnot cycle will be adjusted such that \( W_{\text{cycle}} \) is zero and hence, \( Q_{\text{cycle}} \) is zero, and the negative \( Q \) values exactly balance out the positive \( Q \) values.

\[
Q_{\text{composite}} = Q_1 + Q_2 + Q_3 + \ldots = 0
\]

So that is pretty straight forward. All the exothermic processes should balance out all the endothermic processes. Then the composite cycle will be thermo-neutral, and this condition can be satisfied for any cycle when coupled with an appropriate Carnot cycle.

**14.2.2 Condition 2**

The sum of "\( Q/T \)" terms of the composite cycle should be greater than zero where each term is a ratio of the heat to the corresponding temperature. We also recognize that the temperature is in kelvin, and all \( T \) values are positive.

\[
\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \ldots > 0
\]

While satisfying condition 1, our composite cycle must also satisfy condition 2, above. This is possible only when positive terms out weight negative terms. That is possible when terms with positive \( Q \) values are divided by lower temperature values, and negative \( Q \) values divided by higher \( T \) values. When we divide positive \( Q \)s with low \( T \) values, we get larger values for the positive terms. When we divide negative \( Q \)s with higher temperature values, we get lower value the negative terms. Then, in the sum, the positive terms will dominate the negative terms, and the sum will be greater than zero.

Positive \( Q \)s associated with lower temperature values imply that the system absorbs heat from a low temperature surroundings. Negative \( Q \)s are associated with higher \( T \) values means that heat appears in the surroundings at higher temperatures. This has interesting consequence when the composite cycle operates.

Each time it runs a full cycle certain amount of heat is removed from the surroundings at a lower temperature and certain amount of heat appears at a higher temperature. That is, heat flows from a lower temperature to a higher temperature. That is not an issue by itself, because refrigerators work this way.
However, each time the composite cycle runs, $W_{\text{cycle}}$ is zero. That means, heat should flow spontaneously from a low temperature to high temperature. This is contrary to our experience in the lab or in daily life. Therefore, our assumption for any cycle that the following is valid, is incorrect.

$$\int \frac{dQ}{T} > 0$$

Then, we have two other alternative values: this integral being equal to zero, or less than zero.

$$\int \frac{dQ}{T} \leq 0$$

This is the first part of the proof, it is also lengthier part, and now we divide the second part into two cases, reversible cycles and irreversible cycles.

### 14.2.3 Case 1: Reversible cycles

Thus, our assumption now is that for any reversible cycle, the following must be correct.

$$\int \frac{dQ}{T} < 0$$

This case is simple, the proof is similar to that of the Carnot cycle but the cycle need not need be Carnot cycle and it can be any cycle that is reversible.

Then since this cycle is reversible, we can reverse it and by reversing the cycle we run it backwards. When we reverse the direction of the reversible cycle, the $Q$, and $W$ values of the individual steps will not change, but only their signs will invert. $T$ values do not change either in magnitude or in sign. Then, the above condition will become the following for the reverse direction of the cycle.

$$\int \frac{dQ}{T} > 0$$

When we change all the signs from $-Q$s to $+Q$s and $+Q$s to $-Q$s, then we can conclude that the sign of the integral should change and now it must be greater than zero. But we just showed that for any cycle, reversible or irreversible, this is not possible. It results in the wrong prediction that heat will flow spontaneously from low temperature to high temperature. Therefore, our assumption that this integral is less than zero for any reversible cycle is also wrong. Then the only remaining possible value for the integral for a reversible cycle is the following.

$$\int \frac{dQ_{\text{reversible}}}{T} = 0$$

Since this is a reversible cycle, we can replace the $dQ_{\text{reversible}}/T$ with $dS$, and the cyclic integral is vanishing. We got our proof! Entropy is a state function, after all.

$$\int \frac{dQ}{T} = 0$$

The above is true because we define entropy as $Q_{\text{reversible}}/T$, and show that it is a state function. Since entropy is a state function, we also note, its value does not depend on the path taken, reversible or irreversible, its cyclic integral must vanish, regardless.

Let's say that we have an irreversible cycle and we need to calculate the change in entropy. We will still use the above integral for a reversible cycle, because of the definition of entropy. The change entropy is calculated by constructing a reversible cycle and that integral will vanish. If a change occurs from state one to state two in an irreversible process, then we connect the two states with a reversible process and calculate the entropy change. Even so, we need to examine case II to gain a better understanding of the outcome here.
14.2.4 Case 2: Irreversible cycles

For irreversible cycles the values of Q and W will not necessarily be the same. In fact, we showed that isothermal reversible expansion has the largest magnitude for work compared to one step, two step or other finite step expansions. Similarly, we showed that isothermal reversible compression has the lowest magnitude for work when compared to the corresponding irreversible compression processes. Since cyclic integral of $q_{\text{reversible}}/T = 0$, we will conclude that the following must be correct for all irreversible cycles.

$$\int \frac{dQ_{\text{irreversible}}}{T} \neq 0$$

However, we already showed for any cycle, the following.

$$\int \frac{dQ}{T} \neq 0$$

Then, the only possibility left for any irreversible is the following.

$$\int \frac{dQ_{\text{irreversible}}}{T} < 0$$

In summary, we showed that entropy is a state function because heat can’t spontaneously flow from low temperature to high temperature! To move heat this way, we need to expend work, as in an air conditioning unit or a refrigerator. We could have defined entropy and state that it is a state function as some books do, but the above proof gave us a greater insight into the nature of a natural process and that of entropy. We also showed clearly that the above cyclic integral for all irreversible cycles must be less than zero, a very powerful prediction. Now, we use the above arguments to greater insight into the nature of irreversible process or spontaneous process that we are very much interested in.

14.3 Clausius Inequality

The above proof for entropy led us a very interesting observation and this is elaborated below and the section is divided into two parts for convenience. The first part recognizes the properties of entropy and how it is related to changes during an irreversible process. The second part deals with entropy changes that are occurring in the universe.

14.3.1 Entropy of irreversible processes

Consider any irreversible process. It has the initial state 1 ($p_1$, $V_1$, $T_1$) and final state 2 ($p_2$, $V_2$, $T_2$), connected by an irreversible path, the long blue arrow (Figure 14.3). We design a reversible path from state 2 to state (red curve), which can be purely theoretical and need not be practical but this will become clear soon.
Figure 14.3 Clausius inequality with any irreversible path (blue arrow) from state 1 to state 2. The red line is the reversible path connecting the state 2 back to state 1.

We use the deduction from the previous section for any irreversible cycle, and write the following relation for the irreversible cycle shown in Figure 14.3. Even though the reverse process is reversible, the cycle is not.

\[ \int_{\text{cycle}} \frac{dQ}{T} < 0 \]

We divide this integral in two terms for step 1 (irreversible) plus step 2 (reversible), as following.

\[ \int_{1}^{2} \frac{dQ_{\text{irreversible}}}{T} + \int_{2}^{1} \frac{dQ_{\text{reversible}}}{T} < 0 \]

We use the definition of entropy and write the second integral for the reversible step.

\[ \int_{1}^{2} \frac{dQ_{\text{irreversible}}}{T} + \int_{2}^{1} dS < 0 \]

Flip the sign of the second integral, exchange the limits, so that both integrals have the same initial and final states.

\[ \int_{1}^{2} \frac{dQ_{\text{irreversible}}}{T} - \int_{1}^{2} dS < 0 \]

For an infinitesimal step of this kind, irreversible forward stem and a reversible reverse step, we can write the following in equality where we take the dS term to the other side, leaving the integrals behind.

\[ dS > \frac{dQ_{\text{irreversible}}}{T} \]

What we have now shown is that a reversible path and an irreversible path, both connecting one state to another, and the entropy change dS is greater than \( dQ_{\text{irreversible}}/T \). Now, a clever argument is placed, described below.

Consider a true isolated system, the Universe which we discussed earlier. Since the universe contains both the system and the surroundings, \( dQ_{\text{irreversible}} \) must be zero. Heat can neither leave or enter the isolated system because the surroundings are already included in our system.

\[ dQ_{\text{irreversible}} = 0, \text{isolated system} \]

From the inequality and the above expression, we conclude that, for any process occurring spontaneously, in an isolated system, the entropy change must be positive!

\[ dS > 0, \text{isolated system} \]

This is a very powerful argument and states that all irreversible process or spontaneous process or natural processes occurring in the universe are accompanied by an increase in entropy. This is powerful because it generalizes to all irreversible processes happening anywhere in the universe.

This is the partial answer for our quest, and it is partial only because we need to measure entropy change of the system and that of the system, only then we will get the entropy change of the universe due to our process. This is correct, but bit cumbersome as discussed further, below.

**14.3.2 Entropy is times arrow**

\[ dS > 0, \text{isolated system} \]

The above result is powerful because it can predict if a given chemical reaction can occur spontaneously, just by mixing the reactants for example, or not. Remember we wanted to know if a chemical reaction would take place by itself. Now we claim, yes, the chemical reaction will occur as long as “dS” is greater
than zero for that chemical reaction, when measured with an isolated system or that of the universe. Considering the universe, for us, means we calculate the change in the entropy of the system and also calculate the entropy change in the surrounding and sum them together. It this is greater than zero, then we have a spontaneous reaction taking place. Because of the spontaneous processes happening in our universe, the entropy of the universe is increasing as a function of time. Thus, it is said that entropy is times arrow. Thus, you may find bumper sticker that state 'Entropy is not what it used to be'.

We now have a good predictor to say whether the chemical reaction or a physical process would occur spontaneously, as long as we can measure entropy changes in both the system, surroundings, and the sum is greater than zero. Often times, this kind of analysis is problematic because the analysis includes surroundings and gets more complicated. So, yes, entropy is a good predictor to predict whether that a chemical reaction or a physical process would occur spontaneously but we need to include both the system and the surroundings in our analysis. In a later chapter, we will address this issue, but for now, we are good to go and examine the properties of the new state function, entropy.

### 14.4 Entropy Dependence on p, V, and T

In an independent vein, entropy in its own right is a very important property of the system. Therefore, we are very much interested in figuring out the temperature, pressure, volume dependence of entropy. We use ideal gas as our model to examine these dependencies, because this is a bit more convenient than using real gases for the following derivations.

#### 14.4.1 Entropy Dependence on V and T

We begin our discussions with the volume and temperature dependence of entropy. These are very important variables in many of our experiments because keeping the pressure is of convenience. Many of our derivations will start with the second law of thermodynamics, add the first law and make substitutions as needed, as shown below.

\[
\frac{dT}{S} = \frac{dQ_{rev}}{T}
\]

We substitute for Q in the above, using the first law of thermodynamics, given as below.

\[
dU = dq + dw
\]

\[
T \, dS = dQ_{rev} = dU + p \, dV
\]

This combination of the first and the second laws is very powerful and we could derive a large number of thermodynamic equations from this one equation.

We replace dU in terms of a T-term, using the relation that dU = C_v dT, and write the following.

\[
T \, dS = C_v \, dT + p \, dV
\]

Rearranging and using the ideal gas law, we can write the pV term in two steps, as following.

\[
dS = C_v \left( \frac{1}{T} \right) dT + \left( \frac{p}{T} \right) dV
\]

\[
= C_v \left( \frac{1}{T} \right) dT + \left( \frac{n \, R \, V}{V} \right) dV
\]

The above expression has both the T and V dependencies for an ideal gas, and Cv, n, and R are constants and hence, ready for integration with limits of initial and final states to get the final expression.

\[
\Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) + n \, R \ln \left( \frac{V_2}{V_1} \right), \text{ ideal gas}
\]

In the above, T_1 and T_2 are the temperatures of the initial and final state and V_1 and V_2 are the volumes of the initial and final state volumes, respectively. We conclude from the above relation that entropy an ideal
gas increases with temperature, as well as the volume in a logarithmic fashion. This is illustrated in Figure 14.4.

Figure 14.4 Plot of $\Delta S$ of ideal gas as the logarithmic function of temperature (left, constant volume) and as a function of volume (right, constant temperature). The linear plot on the left has a slope of $C_v$, while the slope of the plot on the right is $nR$. The intercepts are zero in both plots, because when the volume is constant, or when temperature is constant, the corresponding logarithmic term is zero.

This figure teaches us that entropy increases for an ideal gas as we heat it under constant conditions or when we allow it to expand under isothermal conditions. Thus, we can readily connect our previous discussions with entropy, using the above expression.

14.4.2 Entropy as a function of $p$ and $T$

Here, we will examine how the entropy of an ideal gas changes as we change the pressure and temperature. Even though keeping $p$ constant is convenient, we need this variable in some of the high-pressure experiments or in studying may natural process. Thus, pressure is a key variable for us.

We take advantage of the fact that we have derived the temperature-volume relationship and make substitutions using the ideal gas law. We start with the following equation, we just derived.

$$\Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)$$

All we have to do is replace the volume terms with the corresponding pressure terms and we will have the desired equation, and we proceed as follows. For an ideal gas, we recognize that the ratio of volumes is equal to the ratios of the pressure to temperature or as following.

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \frac{p_1}{p_2}$$

Substituting the above relation in the equation for $\Delta S$, we get the following.

$$\Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{T_2}{T_1} \frac{p_1}{p_2} \right)$$

In the next step, we take advantage of the presence of the $C_v$ and $nR$ terms and use the relation $C_p - C_v = nR$ and rearrange to simplify the temperature terms further.

$$\Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) + (C_p - C_v) \left[ \ln \left( \frac{T_2}{T_1} \right) + \ln \left( \frac{p_1}{p_2} \right) \right]$$

Expanding the parenthesis, we get all the five terms and try to cancel some of them, as shown.

$$\Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) + C_p \ln \left( \frac{T_2}{T_1} \right) + C_p \ln \left( \frac{p_1}{p_2} \right) - C_v \ln \left( \frac{T_2}{T_1} \right) - C_v \ln \left( \frac{p_1}{p_2} \right)$$

We recognize that we can cancel the first and the fourth terms, while combining the pressure terms.

$$\Delta S = C_p \ln \left( \frac{T_2}{T_1} \right) + \left( C_p - C_v \right) \ln \left( \frac{p_1}{p_2} \right)$$

We now take advantage of the relation $C_p - C_v = nR$, and simplify further which shows the relation between entropy change, $T$ and $p$ of an ideal gas.
We flip the ratio of pressures to get the alternate expression, as following.

\[ \Delta S = C_p \ln \left( \frac{T_2}{T_1} \right) - n R \ln \left( \frac{p_1}{p_2} \right) \]

The above equation teaches us that a plot of \( \Delta S \) as a function of pressure, at constant T (isothermal process), we will get an exponential decay. Thus, the entropy change will fall off with increase in pressure, exponentially (Figure 14.5). This is in contrast to increase of entropy with volume, we witnessed above. If we plot the log of the pressure, we will get a linear plot with a slope of \(-nR\).

![Figure 14.5 Plot of \( \Delta S \) of ideal gas as the logarithmic function of pressure (left, constant T) and as a function of ln(p) (right, constant T). The exponential plot on the left shows how rapidly entropy falls off with increase in pressure. The linear plot on the right has a slope of \( nR \). The intercept is zero in the linear plot, because when the T is constant, the corresponding logarithmic term is zero.](image)

As we increase the temperature at constant T or V, the entropy of the system increases for an ideal gas. In contrast, entropy decreases with increase in pressure. Thus, we have examined how the entropy changes are influenced by the T, p, and V changes for an ideal gas.

In summary, entropy increases logarithmically with temperature and volume of an ideal gas, while it decreases logarithmically with increase in pressure. The physical significances of these relations will be examined later but first, we will examine another important graph.

**14.4.3 Entropy as a function of T in an isobaric process**

We can impose the constant pressure conditions in the equation we just obtained and examine the temperature dependence of entropy for an isobaric process. We get the following expression and a plot of entropy vs logarithm of temperature for an ideal gas (Figure 14.6) shows a line with slope equal to \( C_p \).

\[ \Delta S = C_p \int_1^2 \frac{1}{T} \, dT \]

\[ \Delta S = C_p \ln \left( \frac{T_2}{T_1} \right) \]
Figure 14.6 Plot of $\Delta S$ of the ideal gas as the logarithmic function of temperature. Entropy increases with temperature in a logarithmic manner with a slope equal to $C_p$, while the slope of the corresponding plot at constant volume conditions was $C_v$.

Thus, entropy increases with $T$ for an ideal gas during an isobaric process and the slope is given as $C_p$. We recognize that slope of a similar plot for an isochoric process gave us a slope of $C_v$. Increased heat capacity of a substance increases the entropy more rapidly with temperature. These entropy changes can be understood readily in terms of energy and space distributions of molecules and this is the focus of the next chapter. Now, however, we will examine other important properties of entropy.

14.5 Standard state of entropy and Coefficients of Expansion and Compression

14.5.1 Standard entropy of an ideal gas

Defining the standard state helps in experimental measurements but we will define this for an ideal gas to demonstrate the implications. The standard state for entropy of an ideal gas is defined as entropy at one atmosphere at some reference temperature (1 atm, constant $T$). Then, we can write $\Delta S$ in terms of the standard state, as follows.

$$\Delta S = S_2 - S^* = -nR \ln(p_2/p_1)$$

$$\Delta S = S_2 - S^* = -nR \ln(p_2/1 \text{ atm})$$

A plot of $S_2 - S^*$, using the standard state, we see that the entropy increases with pressure, as we saw before, except that the initial pressure is 1 atm (Figure 14.7).

![Figure 14.7 Plot of $S_2 - S^*$ for the ideal gas as logarithmic function of pressure, with a slope of $-nR$.](image)

14.5.2 Coefficients of thermal expansion and compressibility

Learning to write the exact differentials and using them for derivations of thermodynamic functions is an important exercise. This approach provides additional insight into the nature of entropy and we obtain additional relations between the quantities we already know and entropy, as following.

Since entropy depends on temperature and pressure for the ideal gas, we would expect $S$ to depend on the coefficients of expansion and compressibility as well. Using the exact differentials, and a length derivation, we can connect these important experimental parameters with entropy.

Since $S$ is a state function, we can write the exact differential $dS$, as following.

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

If we apply constant temperature conditions, as part of our investigation, $dT = 0$, and we have only the volume terms.
We recall the combination of the first and second laws and then construct a parallel equation for \( dS \) at constant \( T \) conditions. The need for this, becomes clear soon,

\[
TdS = dU + p\, dV = C_V\, dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] \, dV
\]

Setting \( dT = 0 \), and rearranging the \( T \) term, we get the desired equation for \( dS \).

\[
dS = \frac{1}{T} \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] \, dV
\]

We compare the equation for \( dS \) from above with the one obtained earlier, and each term on the right of the \( dS \) relation must be equal in both equations. Equating them, we get the following.

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right]
\]

Now we set \( dV = 0 \) in the equation obtained by combining the first and second laws, earlier to get the following.

\[
TdS = C_V\, dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] \, dV, \ \text{set} \ dV = 0
\]

\[
TdS = C_V\, dT
\]

From the above, we write the other important differential function for \( S \) as following.

\[
\left( \frac{\partial S}{\partial T} \right)_V = \frac{1}{T} C_V
\]

These equations by themselves did not give us what we are looking for but a second derivate may be useful to get the coefficients of expansion and compression.

The second derivative of the \( \left( \frac{\partial S}{\partial T} \right)_V \) with respect to \( V \), gives the following expressions.

\[
\frac{d}{dV} \left( \frac{\partial S}{\partial T} \right)_V = \frac{\partial^2 S}{\partial V \partial T} = \frac{d}{dV} \left( \frac{1}{T} \, C_V \right) = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T}
\]

The second derivative of the \( \left( \frac{\partial S}{\partial V} \right)_T \) with respect to \( T \), gives us the following expression.

\[
\frac{d}{dT} \left( \frac{\partial S}{\partial V} \right)_T = \frac{\partial^2 S}{\partial V \partial T} = \frac{d}{dT} \left[ \frac{1}{T} \, \left( \frac{\partial U}{\partial V} \right)_T \right] = \frac{1}{T} \, \left[ \left( \frac{\partial p}{\partial T} \right)_V + \frac{\partial^2 U}{\partial V \partial T} \right] - \frac{1}{T^2} \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right]
\]

Comparing the two double derivatives from above, which should be exactly equal, we get the following new relation.

\[
\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} = \frac{1}{T} \left[ \left( \frac{\partial p}{\partial T} \right)_V + \frac{\partial^2 U}{\partial V \partial T} \right] - \frac{1}{T^2} \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right]
\]

Cancelling the two second derivative terms of \( U \), on both sides of the equation, we get the following.
We have already shown that \( \frac{\partial S}{\partial V} = \frac{1}{T} \left[ p + \frac{\partial U}{\partial V} \right] \), and so, we can substitute left side of this in the above equation, and rearrange it to obtain the relation we seek.

\[
0 = \frac{1}{T} \left( \frac{\partial p}{\partial T} \right)_V - \frac{1}{T^2} \left[ p + \frac{\partial U}{\partial V} \right] 
\]

Since, the subtraction of these two terms is zero, we can safely write the following expression.

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V 
\]

But by definition, we have the following relation, which we arrived much earlier.

\[
\left( \frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa} 
\]

Thus, we can write the following two expressions.

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\kappa} 
\]
\[
dS = \frac{\alpha}{\kappa} dV 
\]

By integrating this expression with limits of the initial (1) and final (2) states, we get the following relation between the quantities we are looking for.

\[
\Delta S = \frac{\alpha}{\kappa} (V_2 - V_1) 
\]

Plot of \( S \) vs \( V \), should give a straight line with a slope equal to \( \alpha/\kappa \) and this is illustrated in Figure 14.8. Compare this with the plot of \( S \) vs \( V \), obtained earlier.

Figure 14.8 Plot of \( S_2 - S^* \) for the ideal gas as logarithmic function of pressure, with a slope of -nR.

Thus, \( S, V, p, \) and \( T \) are related to the heat capacities and the coefficients of thermal expansion and compressibility. Entropy changes can be predicted as a function of pressure, temperature, volume.
14.6 Entropies of Phase Transitions

One of the major experimental measures of entropy involves the phase transitions because these are reversible transformations. Thus, we can measure the entropy changes for these transitions and these values are of high importance for calculating the absolute entropies of substance and the application of the third law of thermodynamics. Phase transitions are carried out usually, under isobaric, isothermal, reversible conditions. They are isothermal because the temperature does not change during the transition until one of the phases is consumed completely.

The equilibrium between the two phases ensures that the transition is reversible. We discussed ice-water equilibrium, when a small amount of the substance is transformed from phase 1 to phase 2 in the forward direction, then a small amount of phase 2 is converted to phase one during the reverse direction, keeping the temperature constant (Figure 14.9).

![Figure 14.8 Phase transitions of ice/water (left) and water/steam (right), at 1 atm and the corresponding transition temperatures.](image)

These transitions are isobaric because, we usually carry these measurements at 1 atm, open to the atmosphere, and hence, the pressure is kept constant automatically at this value.

From the definition of entropy of any process from state 1 to state 2, we write the following expression, where the symbols are as defined earlier.

\[
\Delta S = \int_1^2 \frac{dQ_{\text{reversible}}}{T}
\]

Since this is isothermal process for our phase transition, we write the above by pulling the temperature term out of the integral.

\[
\Delta S = \frac{1}{T} \int_1^2 dQ_{\text{reversible}}
\]

Using the first law, we can write the heat term in terms of internal energy, pressure and volume, as following. Note that we are assuming that all work is pV work, because this is an isobaric process and the external pressure is kept equal to the pressure of the system.

\[
\Delta S = \frac{1}{T} \int_1^2 (dU + p\, dV)
\]

We recognize that the operand is simply dH, under isobaric conditions, and replace with it.

\[
\Delta S = \frac{1}{T} \int_1^2 dH
\]
Upon integration of the expression between the two limits, we get the final expression, relating the entropy change with the enthalpy change and the temperature $T$ where the transition taking place.

$$\Delta S = \frac{\Delta H}{T}$$

The signs on the quantities depend on the direction of the process. For example, if $\Delta H$ is positive as in the case of ice to water phase transition, then $\Delta S$ is also positive because temperature is always positive.

$$\Delta H > 0 \text{ then } \Delta S > 0, \text{ boiling}$$

$$\Delta H < 0 \text{ then } \Delta S < 0, \text{ snowing}$$

If the $\Delta H$ is negative then $\Delta S$ is also negative but for all phase transitions, we can obtain the corresponding entropy changes. These are carried out under isobaric and isothermal conditions, or else the above equation is no longer applicable. When the pressure is 1 atm then these are normal boiling points or normal melting points or normal freezing points etc., Some values of these for selected substance are compared in Table 1.

| Table 1. The enthalpy and entropy changes for a few phase transitions at 1 atm. |
|---------------------------------|-------|------|------|
| Liquid $\rightarrow$ Solid      | Water | Benzene | Mo |
| $\Delta S$ (cal/degree) |       |       |     |
| $\Delta H$ (joules/mole)      |       |       |     |
| T (°C)                         |       |       |     |
| 0                              | 4     | 2500  |

<table>
<thead>
<tr>
<th>Liquid $\rightarrow$ Vapor</th>
<th>Water</th>
<th>Benzene</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta S$ (cal/degree)</td>
<td></td>
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<tr>
<td>$\Delta H$ (joules/mole)</td>
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</tr>
<tr>
<td>T (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>76</td>
<td>5500</td>
<td></td>
</tr>
</tbody>
</table>

One last detail is to discuss the implications of the signs of these above values. When we convert ice to water or most solids to their corresponding liquids, the entropy increases. This is essentially because the molecules in the liquid have a higher degree of freedom to roam around and this freedom increases their entropy. Similar is the situation for the entropy change for boiling. More details of these changes will be presented in the next chapter.

**14.7 The 3rd Law of thermodynamics**

The third law of thermodynamics defines the entropy of a perfectly crystalline pure substance at 0 K and this is important for calculating the absolute entropies of substances at room temperature and 1 at, pressure. Thus, the third law is important for entropy calculations of pure substances which in turn are useful to calculate entropies of reactions from the corresponding elemental states and the stoichiometry of the chemical reaction at hand.

Third Law states that entropy of a perfectly crystalline, pure substance at zero Kelvin is zero. This is a hypothetical state. Because first of all, we argue getting to zero Kelvin itself is not possible. Secondly, we need to a pure perfectly crystalline and we are saying even a minute impurity will contaminate the sample. But for all practical purposes, we can practice the third law of thermodynamics without difficulty. By definition, this is the lowest entropic state a substance could ever hope to achieve. For these reasons, we call these as the absolute entropy values.

Starting from this state defined by the third law at 0 K, we can compute the absolute entropy of any substance at room temperature. We heat the sample up to room temperature, for example, and measure its entropy. We developed the pertinent equations to account for entropy changes due to temperature, volume and pressure. If there are phase changes such as melting or boiling along the way from 0 K to room temperature, we can also obtain the corresponding entropy changes for these phase transitions and add them to the entropy of the substance.
\[
\Delta S = C_{p,\ solid} \int_{0}^{T_{m}} \frac{1}{T} dT + \frac{\Delta H_{m}}{T_{m}} + C_{p,\ liquid} \int_{T_{m}}^{T_{b}} \frac{1}{T} dT + \frac{\Delta H_{b}}{T_{b}} + C_{p,\ gas} \int_{T_{b}}^{T} \frac{1}{T} dT
\]

The first integral accounts for entropy change (\(\Delta S_{1}\)) for heating the sample from 0 K to its melting point (\(T_{m}\)) having a heat capacity of \(C_{p,\ solid}\). The second term accounts for the entropy change (\(\Delta S_{2}\)) due to the phase transition of solid to liquid phase having enthalpy of melting (\(\Delta H_{m}\)) at its melting point (\(T_{m}\)). The third term accounts for the heating of the liquid from its melting point to its boiling point (\(T_{b}\)) with its heat capacity (\(C_{p,\ liquid}\)). The fourth term accounts for the entropy change (\(\Delta S_{4}\)) for the phase transition from the liquid to the gas at its boiling point (\(T_{b}\)) and heat of evaporation (\(\Delta H_{b}\)), and the last term accounts for the heating of the vapor from the boiling point to room temperature with its corresponding heat capacity (\(C_{p,\ gas}\)). We write the corresponding entropy changes for these processes, as following.

- Solid at 0 K \(\rightarrow\) Solid at \(T_{m}\) + \(\Delta S_{1}\) 1
- Solid at \(T_{m}\) \(\rightarrow\) Liquid at \(T_{m}\) + \(\Delta S_{2}\) 2
- Liquid at \(T_{m}\) \(\rightarrow\) Liquid at \(T_{b}\) + \(\Delta S_{3}\) 3
- Liquid at \(T_{b}\) \(\rightarrow\) Vapor at \(T_{b}\) + \(\Delta S_{4}\) 4
- Vapor at \(T_{b}\) \(\rightarrow\) Vapor at \(T\) + \(\Delta S_{5}\) 5

Thus, the absolute entropies are substances or the third law entropies of substances are obtained by summing the above five values.

\[
\Delta S = \Delta S_{1} + \Delta S_{2} + \Delta S_{3} + \Delta S_{4} + \Delta S_{5}
\]

In summary, the third law sets the lowest entropy value for a pure, crystalline substance at 0 K to be zero, and allows us to calculate the absolute entropies of substances in a systematic manner. These entropies for numerous substances at 1 atm are already known.

### 14.8 Molecular interpretation and applications in daily life

**Molecular interpretation**

The molecular description of entropy is quite simple, indeed. It is considered as the degree of disorder, and this aspect will be covered extensively in the next chapter. Here, we will focus the dependence of entropy on pressure, volume, and temperature. Considering that entropy is the degree of disorder, we can readily envision how it decreases with pressure, but increases with volume and temperature. For example, increasing the volume increases the degree of randomness as the gas particles attempt to occupy all the space available to them. But when you increase the pressure or compressing the gas decreases volume at constant temperature, and hence, from the above picture, the degree of disorder decreases. By increasing the temperature at constant volume, or constant pressure, the randomness increases because the particles have higher kinetic energies and traveling faster and faster. Thus, the influence of \(p\), \(V\), and \(T\) on entropy can be readily understood.

Specific heat and entropy are related. Increasing the specific heat increases the entropy. Because you need more energy to raise the temperature to one degree means that there is a greater raise in the kinetic energy of the gas particles, increasing its randomness and hence, its entropy. The greater the heat capacity, the greater the entropy.

The third law of thermodynamics utilizes the high degree of order expected when the substance is pure, perfectly crystalline and at 0 K. When the substance is pure, there are no impurities mixed in the sample, all particles are exactly chemically the same as each other. Thus, pure substances have lower entropy than the impure substances, and this will be established in a later chapter. Analogously, the degree of crystallinity also influences the degree of randomness and hence, a perfectly crystalline does not have this disorder and hence, should have lower entropy than less crystalline but perfectly pure substance. Last but least, the degree of disorder increases with temperature. Since 0 K is the lowest temperature ever attainable, then the lowest degree of disorder is possible only at 0 K and when the substance meets the above three criteria, we have the lowest entropy possible as well. This value is set to zero, because the entropy can’t be any lower than this value, and hence, it has to be zero entropy value for a substance, under these conditions. Thus, the third law allows us to calculate absolute entropies of pure substances at room temperature and pressure by systematic entropy measurements.
Applications in daily Life

A discussed in the previous chapter, entropy increase is associated with all irreversible processes and entropy increase is used in our daily lives for a variety of applications.

14.8.1 Units and worked out examples

Units

Entropy has the SI units of joules/K, and the corresponding base units of kg m^2 s^{-2} K^{-1}.

Worked out example

1. Define the entropy changes happening when the fuel is burned in the gasoline engine to propel your car.

We define the cylinder with fuel filled before the spark plug ignites as the system, and the boundary of the gas as the surroundings. We choose this as an open system so that we can add the fuel, spark the plug and allow the work to appear at the boundary of the system and move the car. As we heat the gases by igniting and burning the fuel with oxygen in the cylinder, entropy of the system is increasing due to the increase in the temperature and also the increase in the mole numbers. For example, gasoline is long chain hydrocarbon and when it is burned in air to produce carbon dioxide and water, the mole numbers are increasing as well.

Increase in the temperature and the mole numbers during the combustion process also increases the pressure of the gases before the piston moves up. We learned that increase in pressure decreases the entropy and the net change in entropy, thus far, depends on the magnitudes of the entropy increases due to the temperature, mole numbers and the pressure.

Volume of the gases is another player that can contribute to entropy. As the gases expand in the cylinder, push the piston, they occupy more space and hence, there is an increase in the entropy of the system due to volume expansion. Thus, the net change in entropy depends on the exact contributions of the above variables to entropy, where at least one of them decrease the entropy of the system.

We also need to consider the surroundings to account for the entropy changes of the universe. This is because, the total entropy change which includes that of the system and the surroundings is a predictor for the natural direction of the combustion process. As the piston moves up and turns the crank shaft of the motor, the wheels turn and the car moves. This process in the surroundings is performing work and increasing the entropy. As the cylinders are firing and recharging with fresh air and fuel, the combustion gases are released into the atmosphere and this also increases the entropy of the surroundings.

In addition to the above changes to entropy to the surroundings, the various motions of the parts convert some of the mechanical energy into heat, raising the entropy of the surroundings. As the car moves, it might crush the pavement, distort the tires and increase the entropy this way as well. Thus, a variety of mechanisms are involved in the process, and include both the system as well as the surroundings that contribute to the total entropy change of the universe. But, we can be certain the total entropy must be >0, as the burning of the fuel and the motion of the car is a spontaneous process or a natural process.

2. Calculate the entropy change when a gas expands in an automobile engine from an initial volume of 200 cc to a final volume of 500 cc, against a constant external pressure of 2 atm, constant temperature of 800 °C, adiabatically. Assume ideal behavior for the gas.

\[ \Delta S = - nR \ln \left( \frac{V_2}{V_1} \right) = - n \ln \left( \frac{500}{200} \right). \]

Assuming ideal gas behavior, \( pV = nRT \) or \( n = \frac{pV}{RT} = 2 \text{ atm} \times 200 \text{ cc} \times (1 \text{ L/100 cc}) / R (800 + 273) \text{ K}. \)

Please substitute the value of \( R \) and calculate \( n \), and insert those in the above expression to get the entropy change.

14.8.2 Key points and terms

Key points

1. General proof for entropy as a state function was obtained by an elaborate method but the key argument was that heat can’t flow spontaneously from a low temperature to high temperature.
2. The above argument is powerful and clearly established entropy as a state function by demonstrating that the cyclic integral of entropy is zero for all reversible cycles.

3. Utilizing the above proof, and constructing an irreversible cycle, the entropy change for an irreversible process is expressed. This is useful for practical applications but it also indicated that the entropy changes occurring in the universe are positive due to the various natural processes happening there.

4. Clausius inequality clearly demonstrated that the entropy changes of irreversible processes are contributing to the increase in the entropy of the universe, and entropy is not what it used to be.

5. Entropy increases exponentially with increase in temperature or increase in volume.

6. Entropy decreases exponentially with increase in the pressure.

7. The third law of thermodynamics states that a pure, perfectly crystalline substances at 0 K have the lowest possible entropy, which can be set to zero.

8. Using the third law, the absolute entropies of substances can be obtained by summing all the entropy changes when the sample is brought from 0 K to room temperature and pressure.

**Key terms**

General proof for entropy as a state function, Clausius inequality, ratio of heat capacities, entropy of the universe, absolute entropies, and the third law of thermodynamics.

**14.8.3 Graphing Assignment**

Plot $S$ vs $T$, $\Delta S$ vs $T$, $\Delta S$ vs $V$ and $\Delta S$ vs $p$ for an ideal gas.

**14.9 Further Reading**

https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-8-second-law/


**14.10 Self Tests**

**14.11 Self Tests Key**
Chapter 15. Entropy and Distributions

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Summary

Entropy is a key thermodynamic property whose role is explored here using special and energy distribution functions. The relation between entropy and the number of ways a system can be arranged is examined in detail and the corresponding expressions derived. Thus, the number of complexions or arrangements are related to the entropy of an ideal gas and the discussions extended to examine the effect of pressure and volume on entropy. The theme is then extended to examine the distribution of energies of the gas particles in the ensemble and related to entropy for understanding the effect of temperature on the entropy of the system. Thus, the connectivity between entropy and the distribution of the particles both in space and energy is examined in detail.

Goals

Probability and its relation to entropy will be explored, first. Then, particular probability models will be constructed to determine the entropy of gases, as they are distributed in a finite volume or volume dependence of entropy will be examined in detail. Quantitative expressions will be constructed to relate the number of ways gas particles can be distributed in a given volume and entropy of the system. Next, our goal is to examine how this expression predicts the effects of volume and pressure on the entropy of the system, in comparison to the expressions we derived in the previous chapter. We will extend these discussions to the space distributions of particles in condensed phases and estimate their entropies. Next, our goal is to relate the energy distribution among the gas particles with entropy and examine the temperature dependence of entropy of the ideal gas. We will close off by reflecting on the relation between entropy and the distribution functions.

15.1 Why Study This?

Entropy is demonstrated to be a key player in predicting if a chemical reaction of a physical process will occur spontaneously, in the previous chapter. This ability of entropy is due to its connection with the way the particles are distributed both in space and energy. Exploring this connectivity between entropy and distribution is key to gain further insight into why entropy is a key factor in driving spontaneous processes. This aspect of entropy and probability is extremely useful in qualitative explanations of why some processes occur spontaneously while others do not. From cocktail conversations to mechanistic investigations can be constructed around the properties of entropy and its dependence on pressure, volume and temperature. This is one of the major reasons to study the current topic. In addition, entropy plays a very important role in our daily lives and understanding this connection help make sense of what is happening in our environment or world of possibilities.

15.2 Probability and Entropy

We will first get a picture of what probability is and then figure out how we can distribute particles in a given volume. We all know that if we buy a lottery ticket, we are likely to win with certain probability. For example, if we buy no tickets there is no chance of winning the lottery. However, if we buy out all the tickets, of course, we sure to win. So, we conclude that the probability of winning the lottery is somehow related to the number of tickets we buy and the number of tickets sold, under ideal conditions, of course.

\[ P = probability\ to\ win = \frac{number\ of\ tickets\ bought}{number\ of\ tickets\ sold} \]

Now, we consider a simple example into how this is applied for a practical example.

15.2.1 Coin toss

We ask, what is the probability that when we toss a coin three times, that heads will show up three times in a row. Now we all know every time you toss the coin there is a 50 percent chance that the head will show up. If we do these three times in a row, each event is independent of the other events, and each event has exactly the same probability of heads showing up 50% of the time. If we do three tossups in a sequence, what is the probability that they had will show up three times in a row. We know for sure that this is not zero, but we also know that this will not happen each time. So, what is the probability of this event happening?
For each tossup, the probability from the above formula is \( \frac{1}{2} \). One out come divided by two possibilities. If we toss the coin twice in a row, then the probability that both tosses will show heads is the product of the probability of the first event and the probability of the second. This is because the two events are independent events and not related. That is, history has no bearing on the outcome. Then, the probability is \( \frac{1}{2} \) multiplied by \( \frac{1}{2} \) and that is \( \frac{1}{4} \).

Now, we compute the probability of tossing three times in a row and obtaining three consecutive appearance of heads. By extension of the above logic, we write that it should be \( \frac{1}{2} \) for each event multiplied by three such events and hence, it will be \( \frac{1}{8} \).

Now we use this approach of calculating independent probabilities for calculating the probability of obtaining a particular distribution or compute total number of possible distributions.

### 15.2.2 Bugs, boxes and entropy

We consider a slightly more complex problem to calculate the probabilities of events happening. Consider three bugs are to be placed in four boxes and we want know how many distinct types we can arrange them. To solve the problem, certain rules are to be applied first. Rule one is that only one bug can occupy each box at any given time, this is called single occupancy mode (Figure 15.1). This is important because we will divide the available volume of the container into small volume cells that will fit just one molecule and not more. Thus, single occupancy is relevant and we acknowledge that no two molecules will be at the same place at the same time.

![Figure 15.1 One of the arrangements of three bugs (blue dots) in four boxes (red squares), chosen randomly.](image)

The second rule is about the identity of any two bugs should be the same. That is, we can’t distinguish between any chosen bug and any other bug in the collection. This is called the identical objects problem. This is also relevant for gas particle model. When the gas is pure, as we normally require, then no two gas particles can be distinguished from each other. Therefore, the second rule that all objects of the collection are identical from each other (Figure 15.1).

Now we work out how many possible ways we can distribute the three bugs in 4 identical boxes but we number them for the sake of counting them. The following approach can be readily implemented to get the answer.

For the first bug, we can choose any of the four boxes, because they are all available and hence, there are found distinct ways to choose the boxes. The second bug can be placed in any of the three remaining boxes and hence, there are three different ways to choose from. The third bug can be placed in any of the two remaining boxes and hence, there are only two choices to pick from.

### 15.2.3 The case of identical bugs and boxes

Thus, the total number of ways to arrange them will be a product of these outcomes, which is \( 4 \times 3 \times 2 \), 24 ways to arrange. But since the 3 bugs are identical, we will soon realize that some of the 24 arrangements are not distinct from the others or some will be counted more than once. That is the three bugs can be arranged among themselves in \( 3! \) ways, and hence the distinct configurations will be \( 24/3! \) or only 4 distinct configurations (Figure 15.2).

Thus, when the objects are identical, as in the case of a pure substance, we have fewer configurations or so-called complexions. Thus, there are only 4 distinguishable ways we can arrange the three bugs in four boxes. We also picked the number of boxes and bugs to be quite similar and this is more like close packing of the particles in a solid or a liquid with very little occupancies left over.
In a gas sample, though, we recognize that there are lot more boxes than the bugs (particles) where each box is the size of a particle, and the entire available volume can be divided into these small boxes. Thus, we will see that we will be examining the two separate scenarios in our later discussions to distinguish between the gases and the condensed phases.

### 15.2.4 Congregational probability

In this case, we will ask a different question. Having worked out how the bugs may be distributed in space, we want to know what is the probability that all the particles will be in one half of the container. That is, we ask what is the probability that the particles condense, spontaneously?

In this case also, we pick identical bugs, but choose only two of them and divide our container into four boxes, where each box can only accommodate one bug. We choose small numbers for both, so that we need not count too many possible ways of distributing them. So, we want to know what is the probability that both bugs will appear on the same side of the 4 boxes of the container and not on opposite ends (Figure 15.3).

![Figure 15.3](image)

Figure 15.3 Distinct configurations of two bugs (blue dots) occupying four boxes (rectangle) in each row, where each bug is identical to any other bug in the collection. We will count how many of the complexions have both bugs on the right half, how many have both on the left, and how many have one on each side.

This is the congregational probability, probability that the bugs will overwhelmingly congregate on one side rather than the other side. We will count the possibilities as shown in Figure 15.3. We place the first bug in the first bug and then place the second one next to it (row 1). Now we keep the first bug in its location and move the second one to the next box (row 2). Then, the second one is now in the third box, then we move it to the fourth box or the last one (row 3).

Now all empty boxes are filled once by bug two. All of these are distinct configurations and ok to count. Now we keep the second bug in the second box and move the first bug to the third box (row 4). Then move it to the last box (row 5). Then, we move the second bug to the third box, keeping the first in the last box (row 6). This way we have created six distinct configurations and there are no more left to make.

For example, two boxes occupy 4 boxes in 4x3 or 12 ways but the two identical boxes can be arranged in 2! Ways among themselves. Thus, there should be only 6 distinct outcomes, as we arrived at. However,
we chose to place them individually and move them around so that we can get a picture of what is where exactly and this is useful for the problem at hand.

We now examine the individual configurations shown in Figure 15.3 and count that there are 2 configurations out of the six that have both the bugs on the same side. Thus, 2 out of 6 configurations have the bugs congregating. There are 4 configurations where each bug is on each side of the container or uniformly distributed.

From these we can summarize that the probability that both bugs will be on the right side is 1 in 6 and the probability that both will be on the left side is 1 in 6, but it's important note that these two be equal because of the unusual symmetry of our box. However, the probability that the bugs will be more uniformly distributed is 4 in 6, much greater than the 1 in 6 of their congregational probability.

So, bugs like to spread out, just as gas molecules, and this is just because of probability not because they like or they hate each other. The probability that the gas particles congregate on just one side is much less than that they will be uniformly distributed. This is analogous to the following example.

Consider a tank of compressed gas, and when the valve is open in the room, the gas molecules will spontaneously and quickly leave the tank and occupy the entire room. We normally never see that gas molecules of a room rush from the room and enter the tank and compress themselves to high pressures. We simply ask why? The above example illustrates the answer. The probability that the gas particles leave the pressurized tank and occupy the room is overwhelmingly larger than the probability that they all will condense or pressurize themselves in a gas tank.

It may appear trivial that this should not be a problem but every day occurrence. But if we think about each molecule each molecule has the equal probability of moving along the x direction or minus x direction plus y direction or minus y direction + z direction or minus z direction. If the directionality of the molecule going left or going right is random right, then why one direction is preferred so all the molecules travel out of the tank and into the room, but not in the opposite direction?

This is referred to as the Boltzmann paradox and that paradox is resolved very nicely using probability or the congregational probability and that's the reason to discuss this example here. There is an overwhelming probability that the gas particles leave a pressurized tank of small volume and occupy the large space of the room, rather than the opposite event. As the room size increases, the number of boxes increase and the probability that bugs will spread out becomes more and more and that the bugs will congregate, become less and less. Natural tendency is to occupy all the space available.

15.2.5 Number of complexions ($\Omega$) and entropy

The above discussion will lead us to calculating the entropy of the system under consideration. The total the total number of possible, distinguishable or unique complexions ($\Omega$) is related to entropy through the Boltzmann constant ($k$), as following

$$S = k \ln \Omega$$

For four identical bugs in 4 identical boxes, there is only one complexion possible, $\Omega = 1$, and $S = 0$. This is analogous to a perfectly crystalline, pure sample at 0 K. The third law states that entropy of the system should be zero, and our calculation from the distributions, in agreement with that.

This relation is powerful, because if we can figure out the total number of bugs and boxes we have, we can precisely calculate the maximum possible distinct configurations and from it the entropy of the system, a wonderful triumph!

15.3 Spatial Distribution and Entropy

We will use the above approach to determine the entropy of a gas occupying a vessel of finite dimensions and volume $V$. We divide the volume of the container of the gas into $m$ boxes, where each box can accommodate only one particle (rule 1) and all particles are identical (rule 2). Since the size of the gas particle being very small, we will have very large number of imaginary boxes in our container. Let there be $N$ number of particles in our gas sample. We get the number of complexions via a systematic approach delineated below, and from it calculate the entropy of our system.
15.3.1 Case 1: Identical boxes, two particles

Let there be just 2 particles and we distribute them into m boxes. The first particle can be placed in any one of the m boxes and the second particle can go into any one of the remaining m-1 boxes. Then, the total number of complexions are m(m-1) but half of these will be identical the other half. Then, the number of unique complexions will be m(m-1)/2. Then, the entropy of the system (S) is k ln [m(m-1)].

\[ \Omega = m(m - 1)/2 \]
\[ S = k \ln \Omega = k \ln (m(m - 1)/2) \]

The value of the logarithmic term will be very large, and hence the entropy of the system will be very high as well. Having worked out this simple case, we now move on to a system of N particles, as following.

15.3.2 Case 2: Identical Boxes, N particles

As before, we have m boxes, N particles and total volume of V liters. The first particle can occupy any one of the m boxes, and hence, it can be arranged m different ways. The second particle can occupy any box out of m-1 remaining boxes and hence, can be arranged in m-1 ways. Then, the third particle can be arranged in m-2 ways, the fourth particle in m-3 ways, and so on. Then, then Nth particle can be arranged in m-N-1 ways. Note that the number of ways of arranging is not m-N ways but m-N-1 ways because the particles that are placed before that used up this many boxes. Thus, the total number of complexions will be product of these terms divided by N!. Because N particles can be arranged among themselves N! ways. Thus, the total number of distinguishable complexes are given as below.

\[ \Omega = \frac{m(m - 1)(m - 2)\ldots(m - (N - 1))}{N!} \]

By multiplying both the numerator and the denominator with (m-N)!, we simplify to the following.

\[ \Omega = \frac{m!}{N!(m-N)!} \]

Entropy is then given simply as below.

\[ S = k \ln \frac{m!}{N!(m-N)!} \]

So that gives us a pretty straightforward, complicated though, expression for entropy. This is the absolute entropy of the system that can be calculated, just using pencil and paper, and that is the strength of physical chemistry. You can sit down and think about it and in your mind's eye, you can work out the observable and then go to the lab test if this is correct.

15.3.3 Physical significance

We ask what are the ramifications of the above expression and what does this really mean to us. We will consider some examples to get a better hold of what is going on here. Let us analyze the total number of distinguishable complexions we got. If we increase the number of boxes (m) while keeping the total number of particles constant, then the terms in the numerator will increase but the denominator stays the same. This change will increase the value of the fraction and hence, will increase the entropy of the system. Increasing the value of m is equivalent to increasing the volume available for the gas to occupy at constant temperature. Thus, increasing the volume increases entropy, which is what we learned in the previous chapter.

\[ \Omega = \frac{m!}{N!(m-N)!} \]

As we keep the number of particles (N) the same, we are keeping the mole numbers the same, and then, the entropy is a function of volume at constant T. Thus, the above formula agrees with our earlier experience. If we decrease m, at constant T, the volume decreases, pressure increases and value of \( \Omega \) decreases and so, entropy decreases. Again, a familiar outcome.

In summary, we constructed a very simple statistical model to determine the number of ways we can prepare the system, or ways we can arrange the gas molecules in a gas container. The logarithm of number of ways of distributing the particles in the volume is related directly to entropy, with a
proportionality constant of k. As \( \Omega \) increases, entropy also increases. As the number of boxes increases, at constant T, the volume increases, Omega increases and entropy increases.

15.3.4 Volume dependence of S – Gases

The dependence of entropy on volume and pressure, as indicated earlier, can be analyzed in terms of number of complexions, in a quantitative manner. We use the general formula, make necessary substitutions for pressure or volume changes and then compare the equations of entropy derived earlier.

We will simplify the above equation for gases by recognizing that the number of volume elements in our gas container (m) are much larger than the number of gas particles (N). This is because a small amount of gas occupies a large volume. There are large gaps between gas molecules at any given time. The actual volume of the gas particles is only a small fraction of the volume of the container, and we discussed this under the kinetic theory of gases.

Under these conditions, we can state that \( m >> N \), such that we can approximate that \( m^{-1} = m, m^{-2} = m, m^{-3} = m, \ldots \) and \( m^{-N} = m \). Under this approximation, we can write the number of complexions as following.

\[
\Omega = \frac{m!}{N!(m-N)!}
\]

We will simplify the above equation for gases by recognizing that the number of volume elements in our gas container (m) are much larger than the number of gas particles (N). This is because a small amount of gas occupies a large volume. There are large gaps between gas molecules at any given time. The actual volume of the gas particles is only a small fraction of the volume of the container, and we discussed this under the kinetic theory of gases.

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\[
\Omega = \frac{m(m)(m)...(m), N\text{ terms}}{N!} = \frac{m^N}{N!}
\]

\[
S = k \ln \Omega = k \ln \left( \frac{m^N}{N!} \right)
\]

\[
S = k (N \ln m - \ln N!)
\]

Now, let the volume increase from the initial volume \( V_1 \) having the number of boxes \( m_1 \) to volume \( V_2 \) with number of boxes \( m_2 \), at constant T. Then \( \Delta S \) is given as below.

\[
\Delta S = k (N \ln m_2 - \ln N!) - k (N \ln m_1 - \ln N!)
\]

Recognizing that the two \( \ln N! \) terms can be cancelled, we obtain the following.

\[
\Delta S = k N (\ln m_2 - \ln m_1) = k N \ln (m_2/m_1)
\]

But, m is proportional to V, so we replace \( m_2/m_1 \) with \( V_2/V_1 \) to obtain the next step.

\[
\Delta S = k N \ln(V_2/V_1)
\]

Now, the desired expression from the last chapter has \( nR \) term and we have \( kN \). So, writing \( N = nM \), where \( n \) is number of moles and \( M \) is the molecular mass, we recognize that \( kN = nR \). The next step is make this change to obtain the final expression.

\[
\Delta S = nR \ln(V_2/V_1)
\]

Thus, starting from the number of complexions, we arrived at the effect of volume on entropy, which is independent of the derivation from the last chapter. Therefore, our expression for \( u \) and its relation with \( S \), must be correct. This is very cool, because we are getting the same result from two very different approaches. Next, we examine the effect of pressure on entropy of gases.

15.3.5 Pressure dependence of entropy - gases

Our approach is similar to that of the above, except that V and T are constant. Then, the pressure will increase only if we increase \( n \). We add more and more gas to the same container, or increase the number of particles to increase pressure. Let the number of particles increase from \( N_1 \) to \( N_2 \). Then, we write the change in entropy as follows.

\[
\Delta S = S_2 - S_1 = k [N_2 \ln m - \ln(N_2)!] - k [N_1 \ln m - \ln(N_1)!]
\]
Grouping the like terms and taking k and \( \ln m \) out, and recognizing that the \( \ln N! \) terms can be a ratio, we get the following simpler relation.

\[
\Delta S = k \left[ (\ln m) (N_2 - N_1) + \ln(N_1!/N_2!) \right]
\]

Since \( m \gg N_1 \) or \( N_2, \) we can consider \( N_1 = N_2, \) and so we are left with only the second term.

\[
\Delta S \sim k \ln(N/N')
\]

We recognize that pressure is proportional to \( N, \) and hence, proportional to \( N! \) and we get the final expression, as following.

\[
\Delta S \sim k \ln(p/p')
\]

Thus, pressure and entropy are inversely related, just as we expected in the previous chapter. Thus, we conclude in this section that our statistical approach agrees well with our previous discussions. Now, we extend these to liquids and solids.

### 15.4 Liquids and Solids

First, the condensed phases have volumes much less than gases, and hence, there is not too much empty space between the particles. Then, \( m \sim N \) or that we can simplify our expression for the number of complexions.

\[
\Omega = \frac{m!}{N!(m-N)!}
\]

\[
\Omega \sim \frac{N!}{N!(N-N)!} \sim 1
\]

Therefore, we conclude that when the number of boxes are nearly the same as the number of particles, our approach indicates that the entropy of the system is much less than that of the gases. This is true, experimentally also. Next, we examine the dependence of entropy on temperature or how it depends on the thermal energy of the system.

### 15.5 Entropy and Energy Distribution

Since temperature is a manifestation of the thermal energy of the system, we need to examine how the energy is distributed among the particles. Thus, if we raise the temperature of the system then more particles will be associated with higher energy than at lower temperature. Thus, we need to examine how the particle distribution among the energy levels at one temperature and then figure out how the distribution would change when we raise or lower the temperature. Therefore, we will construct a ladder or energy levels and then ask how the particles are distributed with respect to energy, instead of volume that we examined in the previous section.

#### 15.5.1 Ladder of discrete energy levels

We will assume that our system has a series of energy levels where each level has a finite amount of energy. That means, if our particle occupies that level, it will have the corresponding amount of energy. We need that these energy levels have different energies, or else all particles will have to go into the same level, and then we can’t increase their energy. Thus, we will have a system of energy levels that our particles can occupy. Next, we assume that the energy spacing between the levels is exactly the same and equal to some value, \( \varepsilon \). This is important and matches with the harmonic oscillator model applied to a thermal oscillator, discussed in the quantum mechanical treatments of oscillators. Along these lines, we will also set the lowest energy level to have non-zero energy or have zero-point energy, as dictated by quantum mechanics. Now, we have a system of energy levels (Figure 15.4) where each vertical red line corresponds to one certain energy level of \( \varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5 \ldots \) etcetera, where each level is separated by energy interval of \( \varepsilon \). The collection of \( N \) particles will occupy with \( n_1 \) particles in level \( \varepsilon_1, n_2 \) particles in level \( \varepsilon_2, \) \( n_3 \) particles in level \( \varepsilon_3 \) and so on. Energy increases from the left to right, as indicated by the blue arrow.
Figure 15.4 Energy levels \((\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \ldots)\) of a collection of \(N\) particles with a uniform separation of \(\varepsilon\) where \(n_1\) particles are present in level \(\varepsilon_1\), \(n_2\) particles in level \(\varepsilon_2\), \(n_3\) particles in level \(\varepsilon_3\) and so on. The total number of particles is \(N\) and total energy of the particles is \(U\).

We need to keep in mind that the total energy of the system \((U)\) is finite and hence, sum of all energies of all particles should be equal to \(U\). We recognize that the energy states are discrete, not continuous. One way to look at this is that you have a bucket of marbles and you need to add them to different cups and there are many ways you can choose the marbles to each cup. One difference between our system and the example of a cup is that we can add as many particles as we desired but there will be still room to add more but that is not the case with our cup. But this difference will not be an issue as long as each cup is large enough to accommodate all the marbles. With this understanding, we proceed to obtain the number of complexes.

15.5.2 Particle distribution into the first energy level

We begin adding particles to each energy level and we start with the first level and calculate the number of ways we can populate this level, first. We realize that level \(\varepsilon_1\) can be filled in different ways with \(n_1\) particles. We can add the first particle to this level and we can choose that one particle from our collection of \(N\) particles. Thus, we can choose that first particle in \(N\) distinct ways and this leaves \(N-1\) particles remaining to be distributed. The second particle can be chosen in \(N-1\) ways to added to first energy level.

Then, the third can be chosen in \(N-2\) ways and so on so forth till the last particle corresponding to \(n_1\) is chosen. That last particle can be chosen \((N-(n_1-1))\). For example, the first particle is chosen in \(N-(1-1) = N\) and the second \(N-(1-2) = N-1\) and so on, thus, the last particle can be chosen in \((N-(n_1-1))\) ways.

Thus, the first level \((\varepsilon_1)\) is filled in \(N (N-1)(N-2)\ldots(N-(n_1-1))\) ways. This way, we will fill the second and subsequent energy levels, as discussed below.

15.5.3 Energy Distribution into the remaining energy levels

After choosing \(n_1\) particles, we only have \(N-n_1\) remaining to be distributed and we start this and pick \(n_2\) particles for the second energy level. We now write each filling for all the levels as following.

The second level \((\varepsilon_2)\) is filled in \((N-n_1)(N-n_1-1)(N-n_1-2)\ldots(N-n_1-(n_2-1))\) ways.

The third level \((\varepsilon_3)\) is filled in \((N-n_1-n_2)(N-n_1-n_2-1)(N-n_1-n_2-2)\ldots(N-n_1-n_2-(n_2-1))\) ways.

The fourth level \((\varepsilon_4)\) is filled in \((N-n_1-n_2-n_3)(N-n_1-n_2-n_3-1)(N-n_1-n_2-n_3-2)\ldots(N-n_1-n_2-n_3-(n_2-1))\) ways, till all \(N\) particles are completely distributed.

We don't really have to know what are all the exact energy levels or know exactly what \(n_1, n_2, n_3 \ldots\) are to get the distribution. This is the beauty of mathematical induction.

15.5.4 Restrictions on the Energy Distribution

The above filling of the states has to satisfy two restrictions we discussed earlier. The total number of particles can't exceed \(N\) and total energy can't exceed \(U\). Total number of particles are to satisfy the condition shown below.

\[
\sum_{i=1}^{N} n_i = N
\]
We calculate the energy associated with the energy level 1 by adding the energies of all the particles in that level and then the next one and the next one and so on. Then we sum all these energies of all the levels and it must be equal to $U$. This approach is demonstrated by the following equation.

$$U = n_1 \varepsilon_1 + n_2 \varepsilon_2 + n_3 \varepsilon_3 + \ldots = \sum n_i \varepsilon_i$$

While satisfying these restrictions, we fill all the particles in the available energy levels. Next, we will compute in how many distinct different ways we can build such a system and that is our number of energy complexions for our system and that defines the entropy arising from the energy distribution.

**15.5.5 Energy Complexions and entropy**

The number of ways the first two energy levels can be populated is the product of the number of ways of choosing the particles to populate both these energy levels, as below.

$$N(N-1)(N-2)\ldots(N-(n_1-1))(N-n_1)(N-n_1-1)(N-n_1-2)\ldots(N-n_1-(n_2-1))$$

The red terms originating from filling up the first level and the green terms coming from filling up the second, and now we can write the entire product for all the N particles residing in all their energy levels, as the product of all the corresponding terms. However, one catch is that some of these are not unique because $n_1$ particles can be distributed among themselves $n_1!$, and the same with particles in other levels as well. Thus, division of the total product of possibilities by this number ensures that each and every microstate we create is distinct. Thus, we write the total number of unique complexions as below.

$$\Omega = \left[\frac{N(N-1)(N-2)\ldots(N-(n_1-1))}{n_1! n_2! n_3! n_4! \ldots}\right] = \left[\frac{(N-n_1) (N-n_1-1) (N-n_1-2) \ldots (N-n_1-(n_2-1))}{(3)(2)(1)}\right]$$

We recognize that the numerator has N products and each term is less than the previous term by 1, and hence, the numerator is equal to $N!$. Using this result, we obtain a simpler expression, as below.

$$\Omega = \frac{N!}{n_1! n_2! \ldots}$$

$$S = k \ln \frac{N!}{n_1! n_2! \ldots}$$

As we increase the temperature of the system, internal energy increases, and we have more particles in the upper energy levels. But we have a constant number of particles, when the gas mass is kept constant. Thus, some particles are moved out of the lower energy levels and put into the upper energy levels.

We recognize that as we redistribute the particles into the upper levels from the lower levels numerator is not changing, because we are not changing the total number of particles, mass is kept constant. So, as you raise the temperature, the only things that are changing are the number of $n_1$, $n_2$, $n_3$, $n_4$ .... in the denominator. We still have the same ladder of energy levels it is not that any new energy levels are being created, some particles are moved out of lower levels and placed in the upper levels.

For example, $n_1$ is decreasing. So, lower energy states are robbed of the particles at the expense of populating higher states, and so populations in the lower levels are decreasing and the populations in the higher levels are increasing. For example, $n_1$ becomes smaller, $n_2$ becomes small $n_3$ becomes... and so on and so forth.

This continue to some point and then at some point the populations begin to climb in some higher states. This makes the denominator smaller, and there will be a wider distribution of the particles. A decrease in the value of the denominator will increase S value, and hence, increase in T increases entropy. So much of an energy from lower particles is to be moved up to generate this sort of thing. This is consistent with the expression we got earlier. This is illustrated by the following equation and by Figure 15.5.

$$\Delta S = n R \ln \left(\frac{T_2}{T_1}\right)$$
Figure 15.5 The change in the energy distribution curves when the temperature is increased from \( T_1 \) to \( T_2 \), where \( T_2 > T_1 \). The curve shifts from left (blue) to the right (red) and the height of the maximum point on the curve is reduced, simultaneously.

The effect of temperature is illustrated, as we discussed earlier. At a lower temperature (\( T_1 \)), we have the blue curve and when the temperature increases (\( T_2 \)), the energy distribution curves shift to the right (red) and the height of the maximum point on the curve is reduced, simultaneously. The curve is broadened by increase in temperature and this is consistent with the shifting of the particles from the lower energy levels to the higher energy levels, we discussed above.

In summary, increasing the temperature of the system, shuffles particles from the lower levels to higher levels, thus broadening the distribution, increasing the number of complexions and thus, results in the increase of entropy of the system.

### 15.5.6 Physical significance

Now, we will distinguish between the spatial distribution and energy distribution. The two distribution functions are different because one describes volume dependence and the other describes the temperature dependence of entropy.

Let's take some examples. Gasses expand spontaneously from a high-pressure region to a low-pressure region. This is our common experience. Wind blowing, hurricanes developing, Cyclones etc. So as the system moves from a high pressure to lower pressure region, in these examples, entropy is increasing. That's because as the expansion occurs, the volume distribution is increasing, the number of complexions are increasing and hence, entropy is increasing. Considering that the universe is a closed system, increase in entropy is a spontaneous process and these processes occur, naturally.

We examine the spontaneous flow of heat from high temperature to low temperature. This is because the loss of heat to a lower temperature space, the heat is dispersed more broadly. We have more states that are being populated. That is, greater spatial distribution of energy is achieved. For example, even when the volume is kept constant, the heat is released in the surroundings and the entropy of the system plus surroundings increases. Entropy of the universe, isolated system, increases and the heat flow is a spontaneous process.

Similarly, why does water flow down the hill and not up the hill, spontaneously? Water flows spontaneously from a higher region to a lower region, and as it flows down the hill, the kinetic energy of the water is increasing and part or most of it is converted to heat, and that heat is absorbed by the surroundings. Thus, the entropy of the system and surroundings is increasing. Thus, it is a spontaneous process. In this manner, we can understand how entropy increase is responsible for spontaneous processes to occur. However, this analysis with entropy is complicated by the fact that we need to pay attention to both the system and the surroundings to measure entropy changes for our analysis of a spontaneous process. Therefore, we continue to search if there is thermodynamic property of the system, and only that of the system, that can predict if a process will be spontaneous or not.

Therefore, even though entropy turns out to be a champion in predicting spontaneous processes occurring in an isolated system, we need a property that can predict spontaneous processes in a closed or open system.

### 15.6 Molecular interpretation and applications in daily life

#### Molecular interpretation
The spatial and the energy randomness that we discussed in this chapter contribute to entropy, in a predictable manner. At the molecular level, the increase in energy of a system, even when volume is not a constant, by increasing its temperature is not a spontaneous process. Even though the increase in temperature increases the energy distribution of the system and its entropy, this is not a spontaneous process because the energy distribution of the particles in the surrounding is decreasing. Thus, we need to consider both the system and the surroundings to predict if the process is spontaneous.

When a gas expands, the interparticle distances are increasing, and thus, the number of boxes available for occupancy by the gas is increasing and hence, the number of complexions are increasing. Thus, the entropy of the system is increasing and the process is spontaneous until it begins to compress the surroundings and an equilibrium is established when the system pressure equals to the force acting on the piston. Thus, the special distribution and energy distributions of both the system and the surroundings need to be taken into account.

**Applications in daily Life**

Entropy and its properties are of importance in daily life, as described above. The flow of water down the hill, the dropping of fruit by the trees, flow of heat from a hot reservoir to cold surroundings etc. When we add milk to our coffee in the morning it spontaneously begins mix and this is an example of another spontaneous process, of course stirring helps speed up the process. Dissolution of solutes such as sugar in the coffee are spontaneous too. Disorder is a spontaneous process and overcoming the disorder is the non-natural process that we need to work on, on a daily basis to overcome. The natural tendency is for our dorm rooms to become disordered.

**15.6.1 Units and worked out examples**

**Units**

The number of complexions has no units.

**Worked out example**

1. Examine entropy changes when hot gases expand during the combustion of the internal combustion engine of a car.

   We define the cylinder with fuel filled before the spark plug ignites and the boundary of the gas separating the surroundings from the system. We choose this as an open system so that we can add the fuel, spark the plug and allow the work to appear at the boundary of the system as the piston moves to expand the gases. We heat the gases by igniting and burning the fuel with oxygen in the cylinder and transfer some energy to the surroundings. As the hot gases expand almost instantly, we can consider this as adiabatic expansion and the piston is moved up during this step, the masses are raised or the crank shaft turns producing power to move the car. Expansion of the gases and increase in temperature due to the heat released during the combustion event increase entropy of the system. The expansion is accompanied by increase in the number of complexions of the volume distribution and the increase in temperature is due to the increase in the energy distribution. There are no significant changes in the entropy of the surroundings. Thus, this combustion process is a spontaneous one. After this step of expansion and rotation of the crank shaft by some angle, the burnt gases are released into the environment (thus, polluting the air around) and certain gas mass is being moved out of the system and into the surroundings. Now, the entropy of the surroundings is increasing.

2. Calculate the number of complexions of arranging 3 identical bugs in 5 identical boxes.

   The first bug can be arranged in 5 ways, the second can be placed in any remaining 4 boxes, and the last in any one of the 3 boxes. Thus, number of distributions are 5x4x3 but the 3 bugs can be arranged in 3! ways, and hence the number of distinct configurations are 60/6 = 10.

**15.6.2 Key points and terms**

**Key points**

1. The definition of probability and the distinct ways of arranging objects are important. We always count non-identical configurations or we call them complexions.

2. The number of distinct ways of arranging n particles in m boxes is given by $\Omega$. 


3. The entropy is given as \( S = k \ln \Omega \) where \( k \) is the Boltzmann constant.

**Key terms**
The number of distinct complexions, entropy, Boltzmann constant.

**15.6.3 Graphing Assignment**
Plot the special distribution curve as the gas expands from a low volume to higher volume, at constant temperature.
Plot the energy distribution curve as the gas is heated from a low temperature to a higher temperature, at constant volume.

**15.7 Further Reading**
https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-8-second-law/

**15.8 Self Tests**

**15.8 Self Tests Key**