Part IV
Entropy

In Part III, we introduced the second law of thermodynamics and applied it to cycles and cyclic devices. In this part, we apply the second law to processes.

- The first law of thermodynamics deals with the property energy and the conservation of it.
- The second law leads to the definition of a new property called entropy. Entropy is a somewhat abstract property, and it is difficult to give a physical description of it. Entropy is best understood and appreciated by studying its uses in commonly encountered processes.

Here we start with a discussion of the Clausius inequality, which forms the basis for the definition of entropy, and continue with the increase of entropy principle. Unlike energy, entropy is a nonconserved property, and there is no such thing as conservation of entropy principle. Next, the entropy changes that take place during processes for pure substances, and ideal gases are discussed, and a special class of idealized processes, called isentropic processes, are examined.
THE CLAUSIUS INEQUALITY

The second law of thermodynamics often leads to expressions that involve inequalities. An irreversible (i.e., actual) heat engine, for example, is less efficient than a reversible one operating between the same two thermal energy reservoirs. Likewise, an irreversible refrigerator or a heat pump has a lower coefficient of performance (COP) than a reversible one operating between the same temperature limits. Another important inequality that has major consequences in thermodynamics is the Clausius inequality. It was first stated by the German physicist R. J. E. Clausius (1822-1888), one of the founders of thermodynamics, and is expressed as

\[ \oint \frac{\delta Q}{T} \leq 0 \]  

That is, the cyclic integral of \( \delta Q / T \) is always less than or equal to zero. This inequality is valid for all cycles, reversible or irreversible.

To demonstrate the validity of Clausius inequality, consider a system connected to a thermal energy reservoir at a constant absolute temperature of \( T_R \) through a reversible cyclic device (see figure below).
The cyclic device receives heat $\delta Q_R$ from the reservoir and supplies heat $\delta Q$ to the system whose absolute temperature at that part of the boundary is $T$ (a variable) while producing work $\delta W_{rev}$. The system produces work $\delta W_{sys}$ as a result of this heat transfer. Applying the conservation of energy principle to the combined system identified by dashed lines yields

$$dE_C = \delta W_C + \delta Q_R$$  \hspace{1cm} 4-2a

where $\delta W_C$ is the total work of the combined system ($\delta W_{sys} + \delta W_{rev}$) and $dE_C$ is the change in the total energy of the combined system. Considering that the cyclic device is a reversible one, we have

$$\frac{\delta Q_R}{T_R} = \frac{\delta Q}{T}$$  \hspace{1cm} 4-2b

(see the Eq. 3-28: $\left(\frac{Q_H}{Q_L}\right)_{rev} = \frac{T_H}{T_L}$)

where the sign of $\delta Q$ is determined with respect to the system (positive if to the system and negative if from the system) and the sign of $\delta Q_R$ is determined with respect to the reversible cyclic device. Eliminating $\delta Q_R$ from 4-2a and 4-2b yields

$$dE_C = \delta W_C + T_R \frac{\delta Q}{T}$$

We now let the system undergo a cycle while the cyclic device undergoes an integral number of cycles. Then the relation above becomes

$$W_C = -T_R \int \frac{\delta Q}{T}$$

since the cyclic integral of energy (the net change in the energy, which is a property, during a cycle) is zero. Here $W_C$ is the cyclic integral of $\delta W_C$, and it represents the net work for the combined cycle.

It appears that the combined system is exchanging heat with a single thermal energy reservoir while involving (producing or consuming) work $W_C$ during a cycle. On the basis of the Kelvin-Planck statement of the second law, which states that no system can produce a net amount of work while operating in a cycle and exchanging heat with a single thermal energy reservoir, we reason that $W_C$ cannot be a work output, and thus it
cannot be a negative quantity. Considering that \( T_R \) is an absolute temperature and thus a positive quantity, we must have

\[
\int \frac{\delta Q}{T} \leq 0
\]

which is the **Clausius inequality**. This inequality is valid for all thermodynamic cycles, reversible or irreversible, including the refrigeration cycles.

If no irreversibilities occur within the system as well as the reversible cyclic device, then the cycle undergone by the combined system will be internally reversible. As such, it can be reversed. In the reversed cycle case, all the quantities will have the same magnitude but the opposite sign. Therefore, the work \( W_C \), which could not be a negative quantity in the regular case, cannot be a positive quantity in the reversed case. Then it follows that \( W_C, \text{int rev} = 0 \) since it cannot be a positive or negative quantity, and therefore

\[
\int \left( \frac{\delta Q}{T} \right)_{\text{int,rev}} = 0
\]

for internally reversible cycles. Thus we conclude that **the equality in the Clausius inequality (Eq.4-1) holds for totally or just internally reversible cycles and the inequality for the irreversible ones**.

**ENTROPY**

The Clausius inequality discussed above forms the basis for the definition of a new property called *entropy*.

To develop a relation for the definition of entropy, let us examine Eq. 4-3 more closely. Here we have a quantity whose cyclic integral is zero. Let us think for a moment what kind of quantities can have this characteristic. We know that the cyclic integral of work is not zero.

Now consider the volume occupied by a gas in a piston-cylinder device undergoing a cycle, as shown below.
When the piston returns to its initial position at the end of a cycle, the volume of the gas also returns to its initial value. Thus the net change in volume during a cycle is zero. This is also expressed as

\[ \int dV = 0 \]

That is, the cyclic integral of volume (or any other property) is zero.

Conversely, a quantity whose cyclic integral is zero depends on the state only and not the process path, and thus it is a property. Therefore the quantity \((\delta Q / T)_{\text{int, rev}}\) must represent a property in the differential form.

Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property entropy. It is designated \(S\) and is defined as

\[ dS = \left( \frac{\delta Q}{T} \right)_{\text{int, rev}} \] (in kJ/K)

Entropy is an extensive property of a system and sometimes is referred to as total.
**entropy.** Entropy per unit mass, designated \( s \), is an intensive property and has the unit kJ/(kg \cdot K). The term **entropy** is generally used to refer to both total entropy and entropy per unit mass since the context usually clarifies which one is meant.

The entropy change of a system during a process can be determined by integrating Eq. 4-5 between the initial and the final states:

\[
\Delta S = S_2 - S_1 = \int_{1}^{2} \left( \frac{\delta Q}{T} \right)_{int, rev}
\]

4-6

Notice that we have actually defined the **change** in entropy instead of entropy itself, just as we defined the change in energy instead of energy when we developed the first-law relation for closed systems.

Absolute values of entropy are determined on the basis of the third law of thermodynamics, which is discussed later.

Engineers are usually concerned with the **changes** in entropy. Therefore, the entropy of a substance can be assigned a zero value at some arbitrarily selected reference state, and the entropy values at other states can be determined from Eq.4-6 by choosing state 1 to be the reference state \( (S = 0) \) and state 2 to be the state at which entropy is to be determined.

So, what is entropy? To answer this, let us ask: what is energy? The point is, do we exactly know what energy is? Perhaps not; we do not need to know what energy is, but we find it satisfactory to interpret internal energy, on the basis of a kinetic molecular hypothesis, as the kinetic and potential energies of atoms and molecules. Similarly, we do not need to know what entropy is, but we find it satisfactory to interpret entropy, on the basis of a kinetic-molecular hypothesis, in terms of the randomness of the distribution of atoms and molecules in space and in energy states.

To perform the integration in Eq. 4-6, one needs to know the relation between \( Q \) and \( T \) during a process. This relation is often not available, and the integral can be performed for a few cases only. For the majority of cases we have to rely on tabulated data for entropy.

Note that entropy is a property, and like all other properties, it has fixed values at fixed states. Therefore, the entropy change \( \Delta S \) between two specified states is the same no matter what path, reversible or irreversible, is followed during a process.
Also note that the integral of $\frac{\delta Q}{T}$ will give us the value of entropy change only if the integration is carried out along an internally reversible path between the two states.

The integral of $\frac{\delta Q}{T}$ along an irreversible path is not a property, and in general, different values will be obtained when the integration is carried out along different irreversible paths. Therefore, even for irreversible processes, the entropy change should be determined by carrying out this integration along some convenient imaginary internally reversible path between the specified states.

**THE INCREASE IN ENTROPY PRINCIPLE**

Consider a cycle that is made up of two processes: process 1-2, which is arbitrary (reversible or irreversible), and process 2-1, which is internally reversible, as shown.
From Clausius inequality,
\[
\int \frac{\partial Q}{T} \leq 0
\]
or
\[
\int_1^2 \frac{\partial Q}{T} + \int_1^2 \left( \frac{\partial Q}{T} \right)_{\text{int,rev}} \leq 0
\]

The second integral in the above relation is readily recognized entropy change \( S_1 - S_2 \). Therefore
\[
\int_1^2 \left( \frac{\partial Q}{T} \right) + S_1 - S_2 \leq 0 \quad 4\text{-7}
\]

which can be rearranged as
\[
\Delta S = S_2 - S_1 \geq \int_1^2 \left( \frac{\partial Q}{T} \right) \quad 4\text{-8}
\]

Equation 4-8 can be viewed as a mathematical statement of the second law of thermodynamics for a closed mass. It can also be expressed in differential form as
\[
dS \geq \frac{\partial Q}{T} \quad 4\text{-9}
\]
where the equality holds for an internally reversible process and the inequality for an irreversible process.
We may conclude from these equations that the entropy change of a closed system during an irreversible process is greater than the integral of $\delta Q/T$ evaluated for that process. In the limiting case of a reversible process, these two quantities become equal. We again emphasize that $T$ in the above relations is the absolute temperature at the boundary where the differential heat $\delta Q$ is transferred between the system and the surroundings.

The quantity $\Delta S = S_2 - S_1$ represents the entropy change of the system which, for a reversible process, becomes equal to $\int_T^2 \frac{\partial Q}{T}$, which represents the entropy transfer with heat.

The inequality sign in the relations above is a constant reminder that the entropy change of a closed system during an irreversible process is always greater than the entropy transfer. That is, some entropy is generated or created during an irreversible process, and this generation is due entirely to the presence of irreversibilities. The entropy generated during a process is called entropy generation, and is denoted by $S_{gen}$. Noting that the difference between the entropy change of a closed system and the entropy transfer is equal to entropy generation, Eq. 4-8 can be rewritten as an equality as

$$\Delta S = S_2 - S_1 = \int_T^2 \frac{\partial Q}{T} + S_{gen}$$  \hspace{1cm} 4-10

Note that entropy generation $S_{gen}$ is always a positive quantity or zero. Its value depends on the process, and thus it is not a property of the system.

Equation 4-8 has far-reaching implications in thermodynamics. For an isolated system (or just an adiabatic closed system), the heat transfer is zero, and Eq. 4-8 reduces to

$$\Delta S_{isolated} \geq 0$$  \hspace{1cm} 4-11

This equation can be expressed as the entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant. In other words, it never decreases. This is known as the increase of entropy principle.

- Note that in the absence of any heat transfer, entropy change is due to irreversibilities only, and their effect is always to increase the entropy.
- Since no actual process is truly reversible, we can conclude that some entropy is
generated during a process, and therefore the entropy of the universe, which can be considered to be an isolated system, is continuously increasing. The more irreversible a process is, the larger the entropy generated during that process.

- No entropy is generated during reversible processes ($S_{gen} = 0$).

Entropy increase of the universe is a major concern not only to engineers but also to philosophers and theologians since entropy is viewed as a measure of the disorder (or "mixed-up-ness") in the universe.

The increase of entropy principle does not imply that the entropy of a system or the surroundings cannot decrease. The entropy change of a system or its surroundings can be negative during a process (see figure); but entropy generation cannot.

The increase of entropy principle can be summarized as follows:

$$\begin{align*}
\Delta S_{sys} &= -2 \text{ kJ/K} \\
S_{gen} &= 3 \text{ kJ/K}
\end{align*}$$

> 0 irreversible process

$S_{gen} = 0$ reversible process

< 0 impossible process

This relation serves as a criterion in determining whether a process is reversible, irreversible, or impossible.
The things in nature have a tendency to change until they attain a state of equilibrium. The increase in the entropy principle dictates that the entropy of an isolated system will increase until the entropy of the system reaches a maximum value. At that point the system is said to have reached an equilibrium state since the increase in entropy principle prohibits the system from undergoing any change of state that will result in a decrease in entropy.

**Some Remarks about Entropy**

In the light of the preceding discussions, we can draw the following conclusions:

1. Processes can occur in a *certain* direction only, not in *any* direction. A process must proceed in the direction that complies with the increase of entropy principle, that is, \( S_{\text{gen}} \geq 0 \). A process that violates this principle is impossible. This principle often forces chemical reactions to come to a halt before reaching completion.

2. Entropy is a *nonconserved property*, and there is *no* such thing as the *conservation of entropy principle*. Entropy is conserved during the idealized reversible processes only and increases during *all* actual processes. Therefore, the entropy of the universe is continuously increasing.

3. The performance of engineering systems is degraded by the presence of irreversibilities, and the *entropy generation* is a measure of the magnitudes of the irreversibilities present during that process. The greater the extent of irreversibilities, the greater the entropy generation. Therefore, entropy can be used as a quantitative measure of irreversibilities associated with a process. It is also used to establish criteria for the performance of engineering devices.

**ENTROPY BALANCE**

The property *entropy* is a measure of molecular disorder or randomness of a system, and the second law of thermodynamics states that entropy can be created but it cannot be destroyed. Therefore, the entropy change of a system during a process is greater than the entropy transfer by an amount equal to the entropy generated during the process within the system, and the *increase of entropy principle* is expressed as
Entropy change = Entropy transfer + Entropy generation

\[ \Delta S_{\text{system}} = S_{\text{transfer}} + S_{\text{gen}} \] 4-12

which is a verbal statement of Eq. 4-10. This relation is often referred to as the entropy balance, and is applicable to any kind of system undergoing any kind of process. The entropy balance relation above can be stated as the entropy change of a system during a process is equal to the sum of the entropy transfer through the system boundary and the entropy generated.

1. Entropy Change

Entropy balance is actually easier to deal with than energy balance since, unlike energy, entropy does not exist in various forms. Therefore, the determination of entropy change of a system during a process involves the evaluation of the entropy of the system at the beginning and at the end of the process, and taking their difference. That is,

\[ \text{Entropy change} = \text{Entropy at final state} - \text{Entropy at initial state} \]

or

\[ \Delta S_{\text{system}} = S_{\text{final}} - S_{\text{initial}} \] 4-13

Note that entropy is a property, and the value of a property does not change unless the state of the system changes. Therefore, the entropy change of a system is zero if the state of the system does not change during the process.

2. Mechanisms of Entropy Transfer

Entropy can be transferred to or from a system in two forms: heat transfer and mass flow (in contrast, energy is transferred by work also).

Entropy transfer is recognized at the system boundary as entropy crosses the boundary, and it represents the entropy gained or lost by a system during a process. The only form of entropy interaction associated with a fixed mass or closed system is heat transfer, and thus the entropy transfer for an adiabatic closed system is zero.

Heat Transfer Heat is, in essence, a form of disorganized energy, and some disorganization (entropy) will flow with heat. Heat transfer to a system increases the entropy of that system and thus the level of molecular disorder or randomness, and heat
transfer from a system decreases it. In fact, heat rejection is the only way the entropy of a fixed mass can be decreased. The ratio of the heat transfer $Q$ at a location to the absolute temperature $T$ at that location is called the \textit{entropy flow} or \textit{entropy transfer}, and is expressed as

$$S_{\text{heat}} = \frac{Q}{T}$$

The quantity $Q/T$ represents the entropy transfer accompanied by heat transfer, and the direction of entropy transfer is the same as the direction of heat transfer since absolute temperature $T$ is always a positive quantity. \textit{Therefore, the sign of entropy transfer is the same as the sign of heat transfer positive if into the system, and negative if out of the system.}

- When two systems are in contact, the entropy transfer from the warmer system is equal to the entropy transfer into the cooler one at the point of contact. That is, no entropy can be created or destroyed at the boundary since the boundary has no thickness and occupies no volume.

- Note that work is entropy-free, and no entropy is transferred with work. Energy is transferred with both heat and work whereas entropy is transferred only with heat.

- The first law of thermodynamics makes no distinction between heat transfer and work; it considers them as \textit{equals}.

- The distinction between heat transfer and work is brought out by the second law: \textit{an energy interaction which is accompanied by entropy transfer is heat transfer, and an energy interaction which is not accompanied by entropy transfer is work.} That is, no entropy is exchanged during a work interaction between a system and its surroundings. Thus only \textit{energy} is exchanged during work interaction whereas both \textit{energy} and \textit{entropy} are exchanged during heat transfer (see figure).
3. Entropy Generation

Irreversibilities such as friction, mixing, chemical reactions, heat transfer through a finite temperature difference, unrestrained expansion, non-quasiequilibrium compression or expansion always cause the entropy of a system to increase, and entropy generation $S_{gen}$ is a measure of the entropy created by such affects during a process.

For a reversible process (a process that involves no irreversibilities), the entropy generation is zero and thus the entropy change of a system is equal to the entropy transfer. Therefore, the entropy balance relation in the reversible case becomes analogous to the energy balance relation, which states that energy change of a system during a process is equal to the energy transfer during that process. However, note that the energy change of a system equals the energy transfer for any process, but the entropy change of a system equals the entropy transfer only for a reversible process.

Entropy Balance for Closed Systems

A closed system involves no mass flow across its boundaries, and its entropy change is simply the difference between the initial and final entropies of the system. The entropy change of a closed system is due to the entropy transfer accompanying heat transfer and the entropy generation within the system boundaries, and Eq. 4-10 is an expression for the entropy balance of a closed system.
\[ \Delta S = S_2 - S_1 = \int_1^2 \left( \frac{\partial Q}{T} \right) + S_{\text{gen}} \quad (4-10) \]

When heat in the amounts of \( Q_k \) is transferred through the boundary at constant temperatures \( T_k \) at several locations, the entropy transfer term can be expressed more conveniently as a *sum* instead of an integral to give

\[ \Delta S = S_2 - S_1 = \sum \frac{Q_k}{T_k} + S_{\text{gen}} \quad \text{(kJ/K)} \quad 4-15 \]

Here the left term is the entropy change of the system, and the sum is the entropy transfer with heat.

The entropy balance relation above can be stated as *the entropy change of a closed system during a process is equal to the sum of the entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries*. It can also be expressed in *rate* form as

\[ \frac{dS}{dt} = \sum \frac{\dot{Q}_k}{T_k} + \dot{S}_{\text{gen}} \quad \text{(kW/K)} \quad 4-16 \]

where \( dS / dt \) is the *rate of change of entropy* of the system, and \( \dot{Q}_k \) is the rate of heat transfer through the boundary at temperature \( T_k \). For an *adiabatic process* \( (Q = 0) \), the entropy transfer terms in the above relations drop out and entropy change of the closed system becomes equal to the entropy generation within the system. That is,

\[ \Delta S_{\text{adiabatic}} = S_{\text{gen}} \quad 4-17 \]

Note that \( S_{\text{gen}} \) represents the entropy generation *within the system boundary* only, and not the entropy generation that may occur outside the system boundary during the process as a result of external irreversibilities. Therefore, a process for which \( S_{\text{gen}} = 0 \) is *internally reversible*, but it is not necessarily *totally reversible*. 

4 - 15
WHAT IS ENTROPY?

It is clear from the previous discussion that entropy is a useful property and serves as a valuable tool in the second-law analysis of engineering devices. But this does not mean that we know and understand entropy well. Because we do not. In fact, we cannot even give an adequate answer to the question, What is entropy? Not being able to describe entropy fully, however, does not take anything away from its usefulness. The discussion below will shed some light on the physical meaning of entropy by considering the microscopic nature of matter.

Entropy can be viewed as a measure of molecular disorder, or molecular randomness. As a system becomes more disordered, the positions of the molecules become less predictable and the entropy increases. Thus, it is not surprising that the entropy of a substance is lowest in the solid phase and highest in the gas phase.

In the solid phase, the molecules of a substance continually oscillate about their equilibrium positions, but they cannot move relative to each other, and their position at any instant can be predicted with good certainty. In the gas phase, however, the molecules move about at random, collide with each other, and change direction, making it extremely difficult to predict accurately the microscopic state of a system at any instant. Associated with this molecular chaos is a high value of entropy.

When viewed microscopically (from a statistical thermodynamics point of view), an isolated system that appears to be at a state of equilibrium may exhibit a high level of
activity because of the continual motion of the molecules. To each state of macroscopic equilibrium there corresponds a large number of possible microscopic states or molecular configurations.

The entropy of a system is related to the total number of possible microscopic states of that system, called *thermodynamic probability* $\Omega$, by the **Boltzmann relation** expressed as

$$ S = k \ln \Omega $$

where $k$ is the Boltzmann constant. Therefore, from a microscopic point of view, the entropy of a system increases whenever the molecular randomness or uncertainty (i.e., molecular probability) of a system increases. Thus, entropy is a measure of molecular disorder, and the molecular disorder of an isolated system increases anytime it undergoes a process.

**Let’s justify Eq. 4-18**

Consider two isolated systems 1 and 2 with entropies $S_1$ and $S_2$ and configurations associated with them $\Omega_1$ and $\Omega_2$ respectively. If these systems are combined into one composite system, each of the $\Omega_1$ configuration may be combined with any one of the $\Omega_2$ configurations of the second system, to give a possible configuration of the state of the composite system. Thus

$$ \Omega = \Omega_1 \Omega_2 \quad 4-19a $$

The entropy of the new system becomes

$$ S = S_1 + S_2 \quad 4-19b $$

However, according to Eq. 4-18, $S_1 = k \ln \Omega_1; \quad S_2 = k \ln \Omega_2$

Thus

$$ S = S_1 + S_2 = k \ln \Omega_1 + k \ln \Omega_2 = k \ln (\Omega_1 \Omega_2) $$

or according to 4-19

$$ S = S_1 + S_2 = k \ln \Omega $$

This justifies the appropriateness of setting $k \ln \Omega$ equal to the entropy.
Example 4- What is the order of magnitude of $\Omega$ for a system having entropy 41.84 J/K?

Answer: $e^{3.03 \times 10^{-24}}$

We have just seen that entropy is a measure of molecular disorder. An increase in entropy indicates an increase in disorder. We can, therefore, say that the second law of thermodynamics is a matter of probability.

In terms of probability, the second law, which tells us that in any process entropy increases, states that those processes occur which are most probable. However, this law in terms of probability does not exclude a decrease in entropy, but the probability is extremely low. It is to be noted that, if an increase of entropy is a probability, there is always a chance that the second law might be broken. The chance that the second law is broken can be calculated. These chances are so small for any macroscopic object that the possibility can be ruled out.

More comments

Molecules in the gas phase possess a considerable amount of kinetic energy. But we know that no matter how large their kinetic energies are, the gas molecules will not rotate a paddle wheel inserted into the container and produce work. This is because the gas molecules, and the energy they carry with them, are disorganized. Probably the number of molecules trying to rotate the wheel in one direction at any instant is equal to the number of molecules that are trying to rotate it in the opposite direction, causing the wheel to remain motionless. Therefore, we cannot extract any useful work directly from disorganized energy.

Now consider a rotating shaft shown below. This time, the energy of the molecules is completely organized since the molecules of the shaft are rotating in the same direction together. This organized energy can readily be used to perform useful tasks such as raising a weight or generating electricity.
Being an organized form of energy, work is free of disorder or randomness and thus free of entropy.

There is no entropy transfer associated with energy transfer as work. Therefore, in the absence of any friction, the process of raising a weight by a rotating shaft (or a flywheel) will not produce any entropy. Any process that does not produce net entropy is reversible, and thus the process described above can be reversed by lowering the weight. Therefore, energy is not degraded during this process, and no potential to do work is lost.

Instead of raising a weight, let us operate the paddle wheel in a container filled with a gas, as shown below.

The paddle-wheel work in this case will be converted to the internal energy of the gas, as evidenced by a rise in gas temperature, creating a higher level of molecular chaos and disorder in the container.

- This process is quite different from raising a weight since the organized paddle wheel energy is now converted to a highly disorganized form of energy, which
cannot be converted back to the paddle wheel as the rotational kinetic energy.

- Only a portion of this energy can be converted to work by partially reorganizing it through the use of a heat engine. Therefore, energy is degraded during this process, the ability to do work is reduced, molecular disorder is produced, and associated with all this is an increase in entropy.

The *quantity* of energy is always preserved during an actual process (the first law), but the *quality* is bound to decrease (the second law). **This decrease in quality is always accompanied by an increase in entropy.**

As an example, consider the transfer of 10 kJ of energy as heat from a hot medium to a cold one. At the end of the process, we will still have the 10 kJ of energy, but at a lower temperature and thus at a lower quality.

Heat is, in essence, a form of disorganized energy, and some disorganization (entropy) will flow with heat. As a result, the entropy and the level of molecular disorder or randomness of the hot body will decrease with the entropy and the level of molecular disorder of the cold body increase. The second law requires that the increase in entropy of the cold body be greater than the decrease in entropy of the hot body, and thus the net entropy of the combined system (the cold body and the hot body) increases. That is, the combined system is at a state of greater disorder at the final state. Thus we can conclude that processes can occur only in the direction of increased overall entropy or molecular disorder.

From a statistical point of view, entropy is a measure of molecular randomness, i.e., the uncertainty about the positions of molecules at any instant. Even in the solid phase, the molecules of a substance continually oscillate, creating an uncertainty about their position. These oscillations, however, fade as the temperature is decreased, and the molecules become completely motionless at absolute zero. This represents a state of ultimate molecular order (and minimum energy). Therefore, **the entropy of a pure crystalline substance at absolute zero temperature is zero** since there is no uncertainty about the state of the molecules at that instant. This statement is known as the **third law of thermodynamics.**

- The third law of thermodynamics provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is called **absolute entropy**, and it is extremely useful in the thermodynamic analysis of chemical reactions.
• Notice that the entropy of a substance that is not pure crystalline (such as a solid solution) is not zero at absolute zero temperature. This is because more than one molecular configuration exists for such substances, which introduces some uncertainty about the microscopic state of the substance.

CALCULATION OF ENTROPY CHANGES

As shown earlier, the change in entropy depends only on the initial and final states of a system, and not on the path taken between the states. If a given process is irreversible (e.g. expansion of a gas into a vacuum) we obtain no value of \( Q_{\text{rev}} \) from which to determine \( \Delta S \) with the help of \( \Delta S = Q_{\text{rev}} / T \); we then try to imagine some path whereby the same final state is achieved reversibly and \( \Sigma (Q_{\text{rev}} / T) \) for this gives the value \( \Delta S \) for the irreversible process. We shall discuss here the methods of calculating entropy changes under different conditions.

Isothermal expansion of an ideal gas into a vacuum

In passing from an initial volume \( V_1 \) to a final volume \( V_2 \), \( n \) mol of the gas change entirely irreversibly without doing any work or absorbing any heat. Nevertheless, as \( S \) is a function of state, the value of \( \Delta S \) for this expansion is exactly the same as the value of \( \Delta S \) for the reversible isothermal expansion of \( n \) mol of the ideal gas from \( V_1 \) to \( V_2 \). We know that for a reversible isothermal expansion

\[
Q_{\text{rev}} = nRT \ln \left( \frac{V_2}{V_1} \right) = nRT \ln \left( \frac{P_1}{P_2} \right)
\]

so

\[
\Delta S = \frac{Q_{\text{rev}}}{T} = nR \ln \left( \frac{V_2}{V_1} \right) = nR \ln \left( \frac{P_1}{P_2} \right)
\]

Where the expansion is in any degree irreversible, both the work done and the heat \( Q_{\text{irrev}} \) absorbed would to that degree be less than those for the reversible expansion, thus
\[
\frac{Q_{rev}}{T} = \Delta S > \frac{Q_{irrev}}{T}
\]

**Example 4-1**

3 mol of an ideal gas is expanded isothermally to five times its initial volume. Calculate the change in entropy.

**Answer**

\[\Delta S \cong 40 \text{ J/K}\]

**Entropy changes at constant volume and at constant pressure**

The equation

\[dU = dQ - P \, dV\]

applies to any system. For a reversible change

\[
\Delta S = \frac{Q_{rev}}{T} = \frac{dU + PdV}{T}
\]

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For a constant volume \(dV = 0\)

\[dS = \frac{dU}{T}\]

or

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

\[C_V = (\partial U / \partial T)_V = T \left( \partial S / \partial T \right)_V\]

Integrating this equation between the temperature limits \(T_1\) to \(T_2\), we get the change in entropy at constant volume due to a change in temperature from \(T_1\) to \(T_2\).

\[
\Delta S = \int_{T_1}^{T_2} C_V \frac{dT}{T} = \int_{T_1}^{T_2} C_V \, d[\ln T]
\]

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Similarly, starting with:
\[ H = U + PV, \]
At constant pressure,
\[ dH = dU + PdV, \]
or from Eq. 4-21
\[ dH/T = (dU + PdV)/T = dS. \]
Thus,
\[ (\partial S/\partial H)_P = 1/T. \]
Since for any system
\[ C_P = (\partial H/\partial T)_P \]
we get
\[ C_P = T(\partial S/\partial T)_P. \]
For a change in temperature from \( T_1 \) to \( T_2 \) at constant pressure, the entropy change is given by
\[ \Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T} = \int_{T_1}^{T_2} C_P d[\ln T] \]
\[ 4-23 \]

**Gibbs paradox**

Let us consider an interesting result. Suppose that 1 mol of an ideal gas A at standard temperature and pressure is allowed to mix isothermally with 1 mol of another ideal gas B at standard temperature and pressure, both having the same initial volume. As the gases are assumed to be ideal, during mixing they move independently of each other.
Therefore, the total change in entropy is the sum of the change in entropy that each gas undergoes individually in the expansion (assuming that the gases were originally confined in two separate containers and allowed to mix together by joining the containers, thus there is an expansion).

Equation 4-20 gives the change in entropy for an isothermal expansion.

\[
\Delta S = R \ln \left( \frac{V_2}{V_1} \right) = R \ln \left( \frac{P_1}{P_2} \right)
\]

According to this equation, gas A has a change in entropy \( R \ln 2 \) and gas B has a change in entropy \( R \ln 2 \). Hence the total change in entropy is \( 2R \ln 2 \).

J. Willard Gibbs noticed that \( \Delta S = 2R \ln 2 \) irrespective of how closely identical the gasses are, provided that they are not the same. Of course, if they are the same, then \( \Delta S \) equals zero. This result is often called the Gibbs paradox. The above result holds for any two different ideal gases mixing together. It should be noted that the change in entropy is associated with change in partial pressure at constant total pressure. If two gases consisting of the same substance mix together, the partial pressure equals the total pressure and remains constant. Hence there is no change in entropy.

Gibbs' paradox is connected with the principle of 'complete indistinguishability of identical fundamental particles' which plays an important role in quantum and statistical mechanics. From his paradox, Gibbs inferred the statistical nature of the entropy.

**Phase change**

Phase changes occur at constant temperature and pressure. If equilibrium conditions are maintained, the process is reversible and

\[
Q_{rev} = Q_P = (\Delta H)_{phase\ change}
\]

Then, from the relation

\[
\Delta S = \frac{Q_{rev}}{T}
\]

we get

\[
\Delta S = \frac{[\Delta H]_{phase\ change}}{T}
\]

that is valid only for phase changes under reversible conditions.
**Example 4-2**
The heat of vaporization of a compound at 27°C was found to be 29.288 kJ/mol. Calculate the molar entropy of vaporization at 27°C.

**Answer:** $\Delta S \approx 98$ J

**Temperature change**
When the temperature of a system is changed, it leads to a change in entropy of that system. To obtain the total entropy change $\Delta S$, we have to add an infinite number of processes, in which an amount of heat $Q_{rev}$ has been absorbed. We know that, for a constant pressure process,

$$Q_P = nC_P \Delta T$$

and this for each infinitesimal step of the process can be written as

$$dQ_P = nC_P dT = dQ_{rev}$$

By combining with

$$\Delta S = Q_{rev} / T$$

we get

$$\Delta S = \int_{T_1}^{T_2} nC_P \frac{dT}{T}$$

This equation can be used to calculate the absolute entropy of a substance.

**a.** If $C_P$ remains constant over the temperature range where there is no phase change, then Equation 4-25 can be written as

$$\Delta S = nC_P \int_{T_1}^{T_2} \frac{dT}{T} = nC_P \ln\left(\frac{T_2}{T_1}\right)$$

**Note:** Although this equation is derived for a reversible path, the same entropy change will result from the transition along any path.
b. If the heat capacity of a system changes with temperature and is given as

\[ C = a + bT + CT^2 + \ldots, \]

the entropy change for heating such a system from a temperature \( T_1 \) to a temperature \( T_2 \) is given by (from Eq. 4-25)

\[ \Delta S = a \ln \left( \frac{T_2}{T_1} \right) + b(T_2 - T_1) + \left( \frac{c}{2} \right)(T_2^2 - T_1^2) + \ldots \]

**Phase changes under non-equilibrium conditions**

For a transition or phase change under non-equilibrium conditions, the entropy change is not given by Equation 4-24. In this case, the entropy change must be calculated by integrating \( dQ/T \) for some reversible means of bringing about the same change in state.

**Example:** Let us consider the isothermal freezing of supercooled water at -5°C. The overall change in state for this can be represented by

\[ \text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (s) \text{ (at -5°C)} \]

Note that supercooled liquid water cannot be reversibly converted, by direct freezing, into a solid at the same temperature. We, therefore, must find some indirect reversible means of bringing about the stated change. One way of doing it is (in three steps):

1. to heat the liquid to 0°C,
2. reversibly freezing it to solid at that temperature, and finally
3. cooling the solid back to -5°C.

Thus, the overall entropy change is

\[ \Delta S = \int_{268K}^{273K} \frac{C_{\text{liquid}}}{T} dT - \frac{(\Delta H)_{\text{fusion}}}{273} + \int_{273K}^{268K} \frac{C_{\text{solid}}}{T} dT = \int_{268K}^{273K} \frac{C_{\text{liquid}} - C_{\text{solid}}}{T} dT - \frac{\Delta H_{\text{fusion}}}{273} \]
THE T-S DIAGRAM

In the second-law analysis, it is very helpful to plot the processes on diagrams for which one of the coordinates is entropy. The two diagrams used most extensively in the second-law analysis are the temperature-entropy and the enthalpy-entropy diagrams.

Consider the defining equation of entropy (Eq. 4-5). It can be rearranged as

$$\delta Q_{int \ rev} = TdS$$  \hspace{1cm} 4-28

As shown in figure below, $\delta Q_{rev}$ corresponds to a differential area on a T-S diagram.

The total heat transfer during an internally reversible process is determined by integration to be
\[ Q_{\text{int\_rev}} = \int_1^2 TdS \]

which corresponds to the area under the process curve on a \( T\)-\( S \) diagram. Therefore, we conclude that \textit{the area under the process curve on a T-S diagram represents the internally reversible heat transfer.}

This is somewhat analogous to reversible boundary work being represented by the area under the process curve on a \( P\)-\( V \) diagram. Note that the area under the process curve represents heat transfer for processes that are internally (or totally) reversible. \textit{It has no meaning for irreversible processes.}

To perform the integrations in Eq. 4-29, one needs to know the relationship between \( T \) and \( S \) during a process. One special case for which these integrations can be performed easily is the \textit{internally reversible isothermal process}. It yields

\[ Q_{\text{int\_rev}} = T_0 \Delta S \]

where \( T_0 \) is the constant temperature and \( \Delta S \) is the entropy change of the system during the process. In the relations above, \( T \) is the absolute temperature, which is always positive. Therefore, heat transfer during internally reversible processes is positive when entropy increases and negative when entropy decreases.

An isentropic process on a \( T\)-\( S \) diagram is easily recognized as a vertical-line segment. This is expected since an isentropic process involves no heat transfer, and therefore the area under the process path must be zero (see figure).
The $T$-$S$ diagrams serve as valuable tools for visualizing the second-law aspects of processes and cycles, and thus they are frequently used in thermodynamics. Below are the $T$-$S$ diagrams for the Carnot, Otto and Diesel cycles.

### Entropy change in the four steps of a Carnot cycle

(See pages 166 – 170 text)

![Diagram of T-S diagram for Carnot cycle]

It can be shown that for a complete Carnot cycle, the work done by the system is equal to the negative of the area enclosed by the cycle.

$$W = - (T_2 - T_1) (S_2 - S_1)$$  \[4-31\]

The area under the rectangle represents a cyclic process and the net heat absorbed by the system in a cycle. According to the first law of thermodynamics this area also represents work. This concept applies only to closed curves. The area between a curve and the $S$ axis does not represent work.
Thermodynamic Definition of Pressure and temperature (the text pages 155 -172)