

PHY215-03: The Second Law of Thermodynamics and Entropy

C.-P. Yuan

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1 Entropy and the Second Law of Thermodynamics

1.1 Entropy

1.1.1 Definition:

Entropy is a thermodynamic quantity that represents the degree of disorder or randomness in a system. It is denoted by the symbol S . In a more precise sense, entropy is related to the number of microscopic configurations or states that a system can adopt while still maintaining the same macroscopic properties. The more possible microstates a system has, the higher its entropy.

1.1.2 Mathematical Expression:

In thermodynamics, the change in entropy ΔS for a reversible process is given by $\Delta S = \frac{Q}{T}$, where Q is the heat transferred to the system and T is the absolute temperature at which the transfer occurs. For an irreversible process, the actual heat transfer dQ and the entropy change are related by the inequality $dS > \frac{dQ}{T}$.

1.1.3 Examples:

For example, when a solid melts into a liquid, the molecules gain more freedom of movement and the system becomes more disordered,

resulting in an increase in entropy. Similarly, when a gas expands into a larger volume, the number of possible positions and momenta of the gas molecules increases, leading to an increase in entropy.

1.2 The Second Law of Thermodynamics

1.2.1 Statement:

The second law of thermodynamics can be stated in several equivalent ways. One common statement is that heat spontaneously flows from a hotter body to a colder body and not in the opposite direction without the input of external work. Another statement is that the entropy of an isolated system always increases or remains constant in a spontaneous process; it never decreases. Mathematically, for an isolated system, $\Delta S \geq 0$.

1.2.2 Implications:

- **Direction of Natural Processes:** It determines the direction in which natural processes occur. Processes that increase the entropy of the universe are spontaneous, while those that would decrease the entropy of the universe are not spontaneous and require external intervention.
- **Limitations on Energy Conversion:** It implies that in any energy conversion process, there is always some energy that is unavailable to do useful work. This is because as energy is transferred or

converted, the entropy of the system and its surroundings increases, and the quality of the energy degrades.

- **Heat Engines:** The second law places fundamental limitations on the efficiency of heat engines. No heat engine can have an efficiency of 100% because some heat must always be rejected to a lower-temperature reservoir to satisfy the increase in entropy requirement.

2 Equivalence of Kelvin-Planck and Clausius Statements of the 2nd Law

In thermodynamics, two statements are "equivalent" if violating one necessarily violates the other—they describe the same fundamental rule (the irreversibility of natural processes) but from different perspectives. Below are the two key proofs of this equivalence:

2.1 Proof 1: If Kelvin-Planck Is Violated, Clausius Is Also Violated

The **Kelvin-Planck Statement** says: No engine can convert all heat from a single reservoir into work (some heat must be rejected).

Suppose we have a Kelvin-Planck Violator (KPV)—an engine that absorbs heat Q_H from a high-temperature reservoir (T_H) and converts all of it to work W_{KPV} , with no heat rejected to a low-temperature reservoir (T_L).

Now pair this KPV with a normal heat pump (a device that uses work to move heat from cold to hot, following Clausius): - The heat pump uses the work W_{KPV} (from the KPV) to absorb heat Q_L from T_L and release total heat $Q_H + Q_L$ to T_H .

Net effect of the combined KPV + heat pump system: - No net work input/output (the KPV's work fully powers the heat pump). - T_L loses Q_L (absorbed by the heat pump). - T_H gains $Q_H + Q_L$ (the heat pump releases more than the KPV absorbs).

This means heat Q_L flows spontaneously from T_L (cold) to T_H (hot) with no external work—directly violating the Clausius Statement.

2.2 Proof 2: If Clausius Is Violated, Kelvin-Planck Is Also Violated

The **Clausius Statement** says: Heat cannot flow spontaneously from cold to hot without external work.

Suppose we have a Clausius Violator (CV)—a device that lets heat Q_L flow spontaneously from T_L (cold) to T_H (hot), no work needed.

Now pair this CV with a normal Carnot engine (follows Kelvin-Planck): - The Carnot engine absorbs heat Q_H from T_H , does work W_{Carnot} , and rejects heat Q_L to T_L (energy conservation:

$$Q_H = W_{Carnot} + Q_L \tag{1}$$

).

Net effect of the combined CV + Carnot engine system: - T_H loses $Q_H - Q_L$ (the engine absorbs Q_H , but the CV returns Q_L). - T_L has no net heat change (the engine rejects Q_L , which the CV sends back to T_H). - The system outputs work W_{Carnot} by using only the net heat $Q_H - Q_L$ from T_H —no heat is rejected to T_L .

This means all heat from a single reservoir (T_H) is converted to work—directly violating the Kelvin-Planck Statement.

Key Takeaway

Since violating either statement forces a violation of the other, the two statements are logically equivalent. They both capture the same “directionality” of nature: heat can’t fully become work, and cold can’t spontaneously heat hot—without tradeoffs.

3 Reversible and Irreversible Thermodynamic Processes

3.1 Reversible Process

- A reversible process is an **idealized** process that can be reversed by an infinitesimal change in some property (e.g., pressure, temperature).
- Both the system and the surroundings return to their **exact initial states** with **no net change** in the universe.
- The process proceeds infinitely slowly, maintaining **thermodynamic equilibrium** (mechanical, thermal, and chemical) at every stage.
- No entropy is generated; the entropy change of the universe is

$$\Delta S_{\text{universe}} = 0.$$

Example: Isothermal expansion of an ideal gas carried out infinitely slowly by keeping the gas in contact with a reservoir and changing the external pressure in infinitesimal steps.

3.2 Irreversible Process

- An irreversible process is a **real** process that cannot be exactly reversed.
- The system and/or surroundings cannot return to their original states without leaving a **net change** in the universe.
- It occurs spontaneously and often rapidly, with finite gradients (temperature difference, pressure difference, etc.).
- Entropy is generated; the entropy change of the universe is

$$\Delta S_{\text{universe}} > 0.$$

Examples:

- Free expansion of a gas into vacuum,
- Heat transfer across a finite temperature difference,
- Natural processes involving friction, viscosity, turbulence, or unrestrained chemical reactions.

Summary

Reversible: ideal, infinitely slow, no entropy generation, $\Delta S_{\text{universe}} = 0$.

Irreversible: real, spontaneous, entropy increases, $\Delta S_{\text{universe}} > 0$.

4 Entropy in a reversible process

In a reversible process, the system and its surroundings can be restored to their original states without leaving any trace of the process. The change in entropy of the system plus the change in entropy of the surroundings is zero. Here are some examples of entropy change in reversible processes:

4.1 Reversible Isothermal Expansion or Compression of an Ideal Gas

4.1.1 Process Description:

An ideal gas is contained in a piston-cylinder device and is allowed to expand or compress at a constant temperature. The process is reversible if it is carried out extremely slowly, with the gas always in thermodynamic equilibrium.

4.1.2 Entropy Change Calculation

For an isothermal reversible expansion of an ideal gas from an initial volume V_1 to a final volume V_2 , the heat transferred Q to the gas is given by $Q = W = nRT \ln \frac{V_2}{V_1}$, where n is the number of moles of the gas, R is the universal gas constant, and T is the absolute temperature. The change in entropy of the gas ΔS is $\Delta S = \frac{Q}{T} = nR \ln \frac{V_2}{V_1}$. If the gas is compressed reversibly from V_2 to V_1 , the

entropy change is $\Delta S = nR \ln \frac{V_1}{V_2} = -nR \ln \frac{V_2}{V_1}$, which means the entropy change of the gas is negative during compression, and the entropy change of the surroundings is positive by the same amount, so the total entropy change of the system and surroundings is zero.

4.2 Reversible Phase Change

4.2.1 Process Description:

Consider a substance that undergoes a phase change, such as water boiling to steam or steam condensing to water, at a constant temperature and pressure. If the heat is supplied or removed in such a way that the process can be reversed at any point, it is a reversible phase change.

4.2.2 Entropy Change Calculation:

During a phase change, the heat transferred $Q = \pm mL$, where m is the mass of the substance and L is the latent heat of the phase change. The plus sign is for absorption of heat (e.g., melting or vaporization) and the minus sign is for release of heat (e.g., freezing or condensation). The change in entropy $\Delta S = \frac{Q}{T} = \frac{\pm mL}{T}$. For example, when water boils at 100°C (373 K) and a mass m of water turns into steam, if the latent heat of vaporization $L = 2260\text{kJ/kg}$, for 1kg of water, the entropy change $\Delta S = \frac{mL}{T} = \frac{1 \times 2260 \times 10^3}{373} \text{J/K} \approx 6060\text{J/K}$. When the steam condenses back to water at the same

temperature, the entropy change of the steam is -6060J/K , and the entropy change of the surroundings is $+6060\text{J/K}$, so the overall entropy change of the system and surroundings is zero.

4.3 Reversible Heat Transfer between Two Bodies with Infinitesimal Temperature Difference

4.3.1 Process Description:

Two bodies with temperatures T_1 and T_2 , where T_1 is slightly higher than T_2 , are brought into contact. Heat is transferred from the hotter body to the colder body in a reversible manner. This requires that the temperature difference $\Delta T = T_1 - T_2$ is infinitesimally small and the heat transfer occurs very slowly.

4.3.2 Entropy Change Calculation:

Let Q be the amount of heat transferred. The entropy change of the hotter body $\Delta S_1 = -\frac{Q}{T_1}$ and the entropy change of the colder body $\Delta S_2 = \frac{Q}{T_2}$. The total entropy change $\Delta S = \Delta S_1 + \Delta S_2 = Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$. As T_1 and T_2 are very close, $\Delta S \approx 0$. In the limit as $\Delta T \rightarrow 0$, the process is reversible and the total entropy change of the system of two bodies and their surroundings is exactly zero.

5 Entropy in an irreversible process

For an irreversible process, the change in entropy (ΔS) is always greater than the heat transfer divided by the temperature. This can be understood through the following aspects:

5.1 General Relationship

- The change in entropy for any process (reversible or irreversible) is defined in terms of a reversible path between the initial and final states. Mathematically, the entropy change is given by $\Delta S = \int \frac{dQ_{rev}}{T}$, where dQ_{rev} is the heat transfer in a reversible process and T is the absolute temperature.

- For an irreversible process, the actual heat transfer dQ and the entropy change are related by the inequality $dS > \frac{dQ}{T}$. This means that the entropy change of the system for an irreversible process is greater than the heat transfer divided by the temperature of the system.

5.2 Entropy Production

- In an irreversible process, there is always some form of dissipation or irreversibility present, such as friction, heat transfer across a finite temperature difference, or diffusion. These processes lead to an

increase in the entropy of the system and its surroundings.

- The total entropy change of the system and its surroundings ($\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$) for an irreversible process is greater than zero, i.e., $\Delta S_{total} > 0$. This increase in total entropy is often referred to as entropy production.

5.3 Examples

5.3.1 Free Expansion of a Gas:

Consider an ideal gas that is initially confined in one part of a container and then allowed to expand freely into an evacuated larger volume. This is an irreversible process. During the free expansion, no heat is transferred to or from the gas ($Q = 0$), and no work is done ($W = 0$). However, the entropy of the gas increases because the gas molecules now have more available volume and thus more possible microstates. The entropy change can be calculated using the formula $\Delta S = nR \ln \frac{V_f}{V_i}$, where n is the number of moles of the gas, R is the gas constant, V_f is the final volume, and V_i is the initial volume.

5.3.2 Heat Transfer Across a Finite Temperature Difference:

When heat flows from a hot body at temperature T_H to a cold body at temperature T_C ($T_H > T_C$), the process is irreversible. The

entropy change of the hot body is $\Delta S_H = -\frac{Q}{T_H}$ (negative because heat is lost by the hot body) and the entropy change of the cold body is $\Delta S_C = \frac{Q}{T_C}$. The total entropy change of the system is $\Delta S = \Delta S_H + \Delta S_C = Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right) > 0$.

In summary, the change in entropy for an irreversible process is characterized by an increase in the total entropy of the system and its surroundings, and it is always greater than what would be calculated based on the heat transfer alone if the process were assumed to be reversible.

6 Reversible engines

In thermodynamics, a reversible engine is an idealized heat engine that operates in a reversible cycle, meaning it can be run in reverse without any loss of energy. The Carnot engine is a theoretical model of this kind.

6.1 Carnot Engine

6.1.1 Working Principle

The Carnot engine operates on the Carnot cycle, which consists of four reversible processes: isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. It uses a working fluid, such as an ideal gas, and exchanges heat with two heat reservoirs at different temperatures, a hot reservoir at temperature T_H and a cold reservoir at temperature T_C .

6.1.2 Efficiency

The Carnot engine is the most efficient reversible engine possible between two given temperatures. It serves as a theoretical benchmark for the maximum efficiency that any heat engine can achieve operating between the same two temperatures, as dictated by the Carnot

efficiency formula:

$$\eta_{\text{Carnot}} \equiv \frac{Q_H - Q_C}{Q_H} = 1 - \frac{T_C}{T_H},$$

because for the Carnot cycle, $\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$. This can be shown by noting that the $Q = nRT \ln(V_f/V_i)$ in the isothermal process and $P_i V_i^\gamma = P_f V_f^\gamma$ in the adiabatic process, with the ideal gas law $PV = nRT$. Furthermore, from energy conservation, the total work done by the system of gas in each cycle is $W_{gas} = Q_H - Q_C$, and the efficiency of the heat engine is defined as $\eta \equiv \frac{W_{gas}}{Q_H}$.

6.1.3 Entropy

In a Carnot engine, the working fluid undergoes a cyclic process consisting of two isothermal and two adiabatic processes. The entropy changes of the working fluid and its surroundings are as follows:

- Change in entropy of the working fluid:

- For the complete Carnot cycle, the entropy change of the working fluid is zero. This is because the Carnot cycle is a reversible cycle. Entropy is a state function, and for a complete cycle that returns the system (the working fluid) to its initial state, the net change in entropy is zero.

- During the isothermal expansion process at temperature T_H (heat source temperature), the working fluid absorbs heat Q_H and the entropy change is $\Delta S_1 = \frac{Q_H}{T_H}$.

- During the adiabatic expansion process, the working substance further expands adiabatically, meaning that no heat is exchanged with the surroundings. The temperature of the working substance drops from T_H to T_C as it works in the surroundings. The adiabatic processes in the Carnot cycle do not change the entropy of the system because there is no heat exchange.
- During the isothermal compression process at temperature T_C (heat sink temperature), the working fluid releases heat Q_C and the change in entropy is $\Delta S_2 = -\frac{Q_C}{T_C}$.
- During the adiabatic compression process, the working substance is compressed adiabatically until it returns to its initial state, with the temperature increasing to T_H . Again, no heat is exchanged with the surrounding. The temperature of the working substance increases from T_C to T_H , and the environment does the same amount of work, as during the adiabatic expansion process.
- For a Carnot engine,

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C},$$
so the net entropy change of the working fluid over the entire cycle $\Delta S = \Delta S_1 + \Delta S_2 = 0$.

- Change in entropy of the surroundings:

- The heat source loses heat Q_H at temperature T_H , so the entropy change of the heat source is $\Delta S_H = -\frac{Q_H}{T_H}$.
- The heat sink gains heat Q_C at temperature T_C , so the change in

entropy of the heat sink is $\Delta S_C = \frac{Q_C}{T_C}$.

- Since $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$, the net entropy change of the surroundings

$$\Delta S_{surr} = \Delta S_H + \Delta S_C = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

for a reversible Carnot cycle.

In summary, for a Carnot engine, both the working fluid and its surroundings have a net entropy change of zero over a complete cycle when the process is reversible.

6.1.4 Statistical Mechanics and Thermodynamics

To derive $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$ for a Carnot engine using statistical mechanics, the following steps can be taken based on the principles of entropy and the Boltzmann distribution. The key lies in relating the heat exchanges and temperatures to the changes in the number of microstates of the system at different temperatures.

- **Entropy and Heat Exchange:**

- In statistical mechanics, the entropy S of a system at thermal equilibrium is given by the Boltzmann formula $S = k_B \ln \Omega$, where k_B is the Boltzmann constant and Ω is the number of microstates of the system.

- For a reversible process, the heat exchange Q with the surroundings is related to the change in entropy ΔS by the equation $\Delta S = \frac{Q}{T}$.

- **The Carnot Cycle in Terms of Microstates:**

- *Isothermal Expansion at T_H :*

When the Carnot engine absorbs heat Q_H from the hot reservoir at

temperature T_H during the isothermal expansion, the system goes from an initial state with Ω_1 microstates to a final state with Ω_2 microstates. The change in entropy ΔS_H is $\Delta S_H = S_2 - S_1 = k_B \ln \frac{\Omega_2}{\Omega_1}$.

From $\Delta S = \frac{Q}{T}$, we have $\frac{Q_H}{T_H} = k_B \ln \frac{\Omega_2}{\Omega_1}$.

- *Isothermal Compression at T_C :*

During the isothermal compression at temperature T_C , the system rejects heat Q_C to the cold reservoir. Let the number of microstates change from Ω_3 to Ω_4 . The change in entropy ΔS_C is $\Delta S_C = S_4 - S_3 = k_B \ln \frac{\Omega_4}{\Omega_3}$, and $-\frac{Q_C}{T_C} = k_B \ln \frac{\Omega_4}{\Omega_3}$. The negative sign indicates that heat is being removed from the system.

- **Connecting the Microstates:**

- Since the Carnot cycle is reversible and the system returns to its original state after a complete cycle, the net change in entropy, which is a state function of the system, must be zero.

- The adiabatic processes in the Carnot cycle do not change the entropy of the system because there is no heat exchange. Hence, the net change in entropy due to the isothermal processes must be zero for a complete cycle, that is $\Delta S_{total} = \Delta S_H + \Delta S_C = 0$.

- $k_B \ln \frac{\Omega_2}{\Omega_1} + k_B \ln \frac{\Omega_4}{\Omega_3} = 0$, which simplifies to $\ln \frac{\Omega_2}{\Omega_1} = -\ln \frac{\Omega_4}{\Omega_3}$, and further to $\frac{\Omega_2}{\Omega_1} = \frac{\Omega_3}{\Omega_4}$.

- **Deriving the Heat-Temperature Relationship:**

- From $\frac{Q_H}{T_H} = k_B \ln \frac{\Omega_2}{\Omega_1}$ and $-\frac{Q_C}{T_C} = k_B \ln \frac{\Omega_4}{\Omega_3}$, and using $\frac{\Omega_2}{\Omega_1} = \frac{\Omega_3}{\Omega_4}$, we

can rewrite $-\frac{Q_C}{T_C} = k_B \ln \frac{\Omega_4}{\Omega_3} = k_B \ln \frac{\Omega_1}{\Omega_2}$.

- Then $\frac{Q_H}{T_H} = k_B \ln \frac{\Omega_2}{\Omega_1}$ and $\frac{Q_C}{T_C} = -k_B \ln \frac{\Omega_1}{\Omega_2} = k_B \ln \frac{\Omega_2}{\Omega_1}$.

- Therefore, $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$.

6.2 Stirling Engine versus Carnot Engine

The Stirling engine is a practical engine, while the Carnot engine is a theoretical one.

6.2.1 Working Principle

- The Stirling engine is a practical engine that operates in a closed regenerative thermodynamic cycle. The Stirling cycle consists of two isothermal processes and two constant-volume processes (regeneration).

6.2.2 Efficiency

- In theory, under ideal conditions (reversible processes and perfect regeneration), the Stirling engine can achieve the same efficiency as the Carnot engine, i.e., $\eta = 1 - \frac{T_C}{T_H}$.

- However, in practice, the Stirling engine's efficiency is lower due to real-world irreversibilities, such as friction, heat losses, and imperfect regeneration.

6.2.3 Entropy

- **Change in entropy of the working fluid:**

- Isothermal processes: In a Stirling engine, there are two isothermal processes. During isothermal expansion at a higher temperature T_H , the working fluid absorbs heat Q_H from the hot reservoir. The entropy change of the working fluid in this process is $\Delta S_1 = \frac{Q_H}{T_H}$. During isothermal compression at a lower temperature T_C , the working fluid releases heat Q_C to the cold reservoir and the change in entropy is $\Delta S_2 = -\frac{Q_C}{T_C}$.

- Regenerator processes: The two other processes in a Stirling cycle are constant-volume processes where the working fluid exchanges heat with the regenerator. Ideally, the regenerator is a perfect heat exchanger and the net heat transfer to and from the working fluid in these processes is zero over a complete cycle. So, the entropy change due to the interaction with the regenerator is zero.

- Net entropy change: For a complete Stirling cycle, if the engine is operating reversibly, the entropy change of the working fluid is zero, because entropy is a state function and the working fluid returns to its initial state after a complete cycle. That is $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_{regen} = 0$, where ΔS_{regen} is the entropy change due to the regenerator processes and is zero.

- **Entropy change of the surroundings:**

- Hot reservoir: The hot reservoir supplies heat Q_H to the working fluid at temperature T_H . So the entropy change of the hot reservoir

is $\Delta S_H = -\frac{Q_H}{T_H}$

- Cold reservoir: The cold reservoir receives heat Q_C from the working fluid at temperature T_C . So the entropy change of the cold reservoir is $\Delta S_C = \frac{Q_C}{T_C}$

- Regenerator: As the regenerator is internal to the engine and ideally does not exchange heat with the surroundings over a complete cycle, it does not contribute to the entropy change of the surroundings.

- Net entropy change: For a reversible Stirling engine, the net entropy change of the surroundings is $\Delta S_{surr} = \Delta S_H + \Delta S_C = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C}$. From the efficiency of the Stirling engine and the first law of thermodynamics, for a reversible operation $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$, so $\Delta S_{surr} = 0$

In an ideal, reversible Stirling engine, both the working fluid and the surroundings have a net entropy change of zero over a complete cycle. However, in a real Stirling engine, due to irreversibilities such as heat transfer losses, friction, and nonideal regenerator operation, the entropy change of the system and the surroundings will be greater than zero, indicating an increase in the overall entropy of the universe.

6.3 A note on Real Engines

In general, real engines are not reversible engines. A few reasons are listed below.

- Friction and Viscosity:

In real engines, there are always frictional forces between moving

parts. For example, in a car engine, the pistons moving in the cylinders experience friction. Friction converts some of the useful work into heat that is dissipated and cannot be recovered to do the work again. Viscous forces in the working fluid also cause energy losses. These irreversible processes lead to a decrease in the overall efficiency of the engine and prevent it from being reversible.

7 The third law of thermodynamics

7.1 Statement:

The third law of thermodynamics states that as the temperature of a system approaches absolute zero, the entropy (or disorder) of the system approaches a minimum value.

- In simpler terms, it means that It is impossible to reach the absolute zero temperature (0 Kelvin) in a finite number of steps. Namely, no matter how many cooling processes or operations are carried out, it is impossible to cool a system exactly to absolute zero (0 K).
- In other words, we can get very close to absolute zero, but we can never actually reach it. Absolute zero is more of an unattainable limit.

7.1.1 Nernst Heat Theorem:

As absolute zero is approached, the entropy change ΔS for a chemical or physical transformation approaches 0. Mathematically, it can be expressed as $\lim_{T \rightarrow 0} \Delta S = 0$, where S represents entropy and T is the temperature.

7.2 Entropy in statistical mechanics

- At absolute zero temperature, the system is in the state with the minimum thermal energy, the ground state.

- Entropy reaches zero only when the system has a unique ground state (i.e., the state with the minimum thermal energy has only one configuration, or microstate).
- Microstates are used here to describe the probability of a system being in a specific macroscopic state.
- At thermal equilibrium, each microstate has the same probability of occurring, the macroscopic states with fewer microstates are less probable. The entropy of the system is related to the number of possible microstates according to the Boltzmann principle

$$S = k_B \ln \Omega,$$

where S is the entropy of the system, k_B is the Boltzmann constant, and Ω the number of microstates.

- At absolute zero temperature, there is only 1 microstate possible for a perfect crystal. Hence, $\Omega = 1$, and $S = \ln(1) = 0$.
- The entropy of a perfect crystal approaches zero as the temperature approaches absolute zero.
- The concept of absolute zero is the lowest limit of temperature in thermodynamics.
- Based on the Nernst heat theorem, it can be inferred that the heat capacity of a substance approaches zero as the temperature approaches absolute zero. Hence, the thermal motion of particles in the system is extremely weak, and the ability of the system to absorb or release heat is almost lost, which is an important feature of the system at absolute zero.

8 The application of Statistical Mechanics in Thermodynamics

The statistical mechanics was applied to establish a connection between the physics of microscopic systems and macroscopic thermodynamics, providing a theoretical basis for understanding the behavior of matter at the microscopic level.

8.1 Core Concepts

- **Macrostate and Microstate:**

A macrostate represents the overall characteristics of a microscopic system, such as its total energy. In contrast, a microstate details the specific motion states of particles within that system. Multiple microstates can correspond to the same macrostate. A microcanonical ensemble consists of microstates with identical energy levels. In thermal equilibrium, each microstate has an equal probability of occurrence, adhering to the ergodic hypothesis. It suggests that a system will eventually explore all accessible states given enough time. Note that thermal equilibrium occurs when the probability distribution of a system becomes time independent.

– **Boltzmann Distribution:**

When a system reaches thermal equilibrium, the Boltzmann distribution describes the probability of the system being in a specific microstate, which is related to the number of microstates in the en-

vironment. Its formula is

$$p(E_i) = \frac{1}{Z} e^{-\beta E_i},$$

where

$$\beta = \frac{1}{k_B T},$$

with k_B being the Boltzmann constant.

The partition function

$$Z = \sum_i e^{-\beta E_i},$$

which is a fundamental concept in statistical mechanics. It encapsulates information about all the microstates of a system at thermal equilibrium and their corresponding probabilities. Various statistical quantities of the system can be calculated by taking the derivative of its logarithm.

8.2 Important Theories

– Entropy and Temperature:

Entropy

$$S = k_B \ln \Omega$$

is used to measure the diversity of microstates in a system. Temper-

ature is defined as

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{\partial \ln(\Omega(E))}{\partial E}.$$

This definition is consistent with the physical intuition that heat flows from high-temperature to low-temperature regions and also conforms to the zeroth law of thermodynamics.

- **Ensemble Theory:**

The canonical ensemble includes all possible microstates of a system when it is in thermal equilibrium with its environment, with a fixed number of particles. Also, time averages and ensemble averages are equivalent for an ergodic system.

8.3 Applications

- **Calculation of Statistical Quantities:**

Using the partition function, statistical quantities such as the average energy

$$E = -\frac{d \ln Z}{d\beta},$$

and the pressure

$$P = \frac{1}{\beta} \frac{d \ln Z}{dV}$$

can be calculated by taking the ensemble averages

$$X \equiv \langle X_i \rangle = \sum_i p(E_i) X_i,$$

for X being E or P , etc.

- **The Laws of Thermodynamics:**

The three laws of thermodynamics can be written as

(1)

$$dE = TdS - PdV, \quad \text{with} \quad Q = TdS \quad \text{and} \quad W = PdV,$$

(2)

$$\Delta S \geq 0,$$

(3)

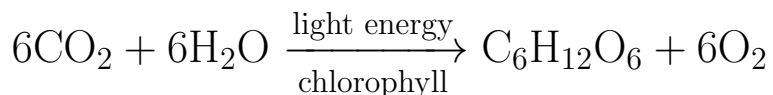
$$T \rightarrow 0 \quad \Rightarrow \quad S \rightarrow 0.$$

9 Photosynthesis and entropy increase

9.1 Photosynthesis

Photosynthesis is a chemical process where plants, algae, and certain bacteria use sunlight, water, and carbon dioxide to create oxygen and sugar (glucose), essentially "making their own food" by converting light energy into chemical energy that can be used by the organism; this process is vital for life on Earth as it produces the oxygen we breathe.

The chemical reaction for photosynthesis in plants can be represented by the following equation:



Explanation:

- Reactants: Carbon dioxide (CO_2) and water (H_2O), which are absorbed by plants through their leaves and roots, respectively.
- Conditions: The reaction requires light energy (captured by the pigment chlorophyll in chloroplasts) and the presence of chlorophyll (found in plant cells).
- Products: Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, a sugar used for energy and growth) and oxygen (O_2 , released as a byproduct into the atmosphere).

This process converts light energy into chemical energy stored in glucose, forming the basis of the food chain and oxygen supply for most life on Earth.

9.2 The relationship between photosynthesis and entropy increase

The relationship between photosynthesis and entropy increase is complex and can be understood from the following aspects:

9.2.1 Photosynthesis as a Local Entropy-Decreasing Process

- Energy Conversion and Order Creation:

Photosynthesis is a process by which plants, algae, and some bacteria convert light energy from the Sun into chemical energy stored in the bonds of organic molecules like glucose. In this process, carbon dioxide and water are taken in and assembled into more complex and organized organic compounds. From a thermodynamic perspective, this represents a decrease in entropy locally. The random molecules of carbon dioxide and water are converted into more ordered and structured organic substances, reducing the degree of disorder.

- Example:

Consider a plant leaf. Inside the chloroplasts, the process of photosynthesis takes disordered molecules and arranges them into the

highly ordered structure of glucose. This is similar to taking a pile of building blocks (disordered) and assembling them into a specific building (ordered), which is a decrease in entropy within the system of the plant.

9.3 Entropy Increase in the Larger Context

- **Energy Dissipation:**

Although photosynthesis itself leads to a decrease in entropy within the plant or photosynthetic organism, it does not violate the second law of thermodynamics, which states that the total entropy of an isolated system always increases over time. This is because the process of photosynthesis requires an input of energy from the Sun. The Sun is constantly radiating energy into the universe, and this energy transfer is associated with an overall increase in entropy. The light energy that drives photosynthesis is part of a larger energy flow in the universe, and the net effect is still an increase in the total entropy of the universe.

- **Heat Release:**

During photosynthesis, not all of the absorbed light energy is converted into chemical energy. Some of the energy is dissipated as heat. This heat release contributes to an increase in the entropy of the surroundings. For example, if you consider a plant in a room, the heat given off by the plant during photosynthesis slightly increases the disorder of the air molecules in the room, increasing the entropy of

the surrounding environment.

In summary, photosynthesis is a process that results in a local decrease in entropy within the photosynthetic organisms as it creates order and stores energy in organic compounds. However, when considering the entire system including the Sun and the surroundings, the overall effect is still in line with the second law of thermodynamics, with the total entropy of the universe increasing due to the energy flow and heat dissipation associated with the process.

The direction of thermal energy transfer is not determined by energy conservation but by the change in entropy of a closed system, with $\Delta S \geq 0$.