LAWS OF THERMODYNAMICS

System, Surroundings, Boundary

- **System:** The specific part of the universe we are interested in studying.
- It can be anything: a gas in a cylinder, a human body, a star.
- **Surroundings:** Everything outside the system that can interact with it.
- The rest of the universe, essentially.
- **Boundary:** The real or imaginary surface that separates the system from its surroundings

- Types of Systems based on Boundary interaction:
- Open System: Exchanges both matter and energy with surroundings (e.g., boiling pot without lid).
- Closed System: Exchanges energy but NOT matter with surroundings (e.g., sealed pressure cooker).
- Isolated System: Exchanges NEITHER matter nor energy with surroundings (e.g., ideal thermos flask)

State, Process, Equilibrium

- **State of a System:** Defined by its macroscopic properties (temperature, pressure, volume, composition).
- These properties are called "state variables" or "state functions."
- The change in a state function depends only on the initial and final states, not the path taken.
- **Process:** A change in the state of a system.
- **Types of Processes:** Isothermal (constant temperature), Isobaric (constant pressure),
- Isochoric (constant volume), Adiabatic (no heat exchange).

- Equilibrium: A state where there are no unbalanced forces or potentials within the system or between the system and surroundings.
- Thermal Equilibrium: Uniform temperature throughout.
- Mechanical Equilibrium: Uniform pressure throughout.
- Chemical Equilibrium: No net change in chemical composition.

Introducing the Zeroth Law of Thermodynamics

- **Discovery:** Formulated after the First and Second Laws, but it's more fundamental, hence "Zeroth."
- **Purpose:** Establishes the concept of temperature as a measurable quantity.
- **Analogy:** Think of it as a logical prerequisite for defining temperature and heat transfer.
- **Foundation:** It's the basis for how thermometers work.

What is Thermal Equilibrium?

- **Definition:** Thermal equilibrium is a state where there is no net flow of heat between two objects or systems in contact.
- **Temperature Equality:** When two objects are in thermal equilibrium, they have the same temperature.
- **Heat Flow:** Heat naturally flows from a hotter object to a colder object until thermal equilibrium is reached.
- **No Change:** Once in thermal equilibrium, their temperatures remain constant over time.

The Zeroth Law

- **Statement:** If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.
- **Simplified:**
- If System A is in thermal equilibrium with System C.
- And System B is also in thermal equilibrium with System C.
- Then, System A and System B are in thermal equilibrium with each other.
- **Logical Implication:** This means that A, B, and C all share the same "property" – temperature.

Importance and Application of Zeroth Law

- **Foundation of Temperature:** Provides a clear definition of temperature.
Temperature is the property that two objects have in common when they are in thermal equilibrium.
- **How Thermometers Work:**
- A thermometer (System C) is placed in contact with an object (System A) until thermal equilibrium is reached.
- The thermometer then has the same temperature as System A.
- When the same thermometer is placed in contact with another object (System B) and shows the same reading, it implies that System A and System B have the same temperature.

Introducing the First Law of Thermodynamics

- **Core Principle:** It is essentially the law of conservation of energy applied to thermodynamic systems.
- **Energy cannot be created or destroyed:** It can only be transformed from one form to another.
- **Historical Context:** Developed in the mid-19th century.
- **Quantitative Relationship:** Relates heat, work, and the internal energy of a system.

Energy: Forms and Transformations

- **Internal Energy (U):** The total energy contained within a system due to the motion and configuration of its molecules.
- Includes kinetic energy (molecular motion) and potential energy (intermolecular forces).
- **Heat (Q):** Energy transferred between a system and its surroundings due to a temperature difference.
- A "process" of energy transfer, not a property of the system.
- **Work (W):** Energy transferred between a system and its surroundings due to a force acting over a distance.
- Examples: expansion/compression of gas, electrical work.
- Also a "process" of energy transfer.
- **Other Forms:** Mechanical, electrical, chemical, nuclear, radiant energy.

Internal Energy (U)

- **Microscopic View:** The sum of all the kinetic and potential energies of the particles (atoms, molecules) within a system.
- **Kinetic Energy:** From translational, rotational, and vibrational motions of molecules.
- **Potential Energy:** From intermolecular forces and intramolecular bonds.
- **State Function:** Internal energy is a state function. Its value depends only on the current state of the system (e.g., temperature, pressure, volume), not on how that state was reached.
- **Change in Internal Energy (ΔU):** The difference between the internal energy of the final state and the initial state.

Work (W) in Thermodynamics

- Definition: Work in thermodynamics refers to energy transfer that is not due to a temperature difference.
- Common Type: Pressure-volume (PV) work, especially for gases.
- Expansion: When a gas expands, it does work *on the surroundings* (W is negative for system).
- Compression: When the surroundings compress a gas, work is done *on the system* (W is positive for system).
- Other Types: Electrical work, shaft work, surface tension work.
- Path Function: Unlike internal energy, work is a path function. The amount of work done depends on the specific path (process) taken between the initial and final states.

Heat (Q) in Thermodynamics

- **Definition:** Heat is the transfer of thermal energy between a system and its surroundings due to a temperature difference.
- **Direction:** Heat flows spontaneously from a region of higher temperature to a region of lower temperature.
- **Modes of Heat Transfer:**
- **Conduction:** Through direct contact (e.g., touching a hot stove).
- **Convection:** Through fluid movement (e.g., boiling water).
- **Radiation:** Through electromagnetic waves (e.g., heat from the sun).
- **Path Function:** Like work, heat is a path function. The amount of heat transferred depends on the specific process undergone by the system.

First Law Equation: $\Delta U = Q - W$

- **Mathematical Statement:** The change in the internal energy (ΔU) of a closed system is equal to the heat (Q) added to the system minus the work (W) done *by* the system.
- **Sign Conventions (Crucial!):**
- **Q (Heat):**
  - $Q>0$: Heat added *to* the system.
  - $Q<0$: Heat removed *from* the system.
- **W (Work):**
  - $W>0$: Work done *by* the system on the surroundings (e.g., expanding gas).
  - $W<0$: Work done *on* the system by the surroundings (e.g., compressed gas).

Applications of the First Law

- **Power Plants:** Describes how heat energy from fuel combustion is converted into mechanical work to generate electricity.
- **Internal Combustion Engines:** Explains how the burning of fuel (ΔU, Q) pushes pistons (work W).
- **Refrigerators and Heat Pumps:** Energy is conserved, but specific processes are needed to move heat against a temperature gradient (related to the Second Law).
- **Biological Systems:** Energy balance in living organisms (metabolism).
- **Any Process with Energy Transformation:** The First Law is a fundamental accounting principle for energy.

Introducing the Second Law of Thermodynamics

- **Beyond Conservation:** While the First Law tells us energy is conserved, it doesn't tell us *if* a process will happen or *in what direction*.
- **The "Why":** The Second Law addresses the natural direction of processes and why certain energy transformations are not 100% efficient.
- **Spontaneity:** It helps predict whether a process will occur spontaneously.
- **Efficiency Limits:** Sets theoretical limits on the efficiency of heat engines and refrigerators.
- **Key Concept:** Introduces the concept of Entropy.

Limitations of the First Law

- **No Directionality:** The First Law doesn't specify the direction of a process.
- Example: Heat flowing from hot to cold is spontaneous, but the First Law wouldn't forbid heat flowing from cold to hot (it would just say energy is conserved).
- **No Information on Feasibility:** It doesn't tell us if a process is actually possible.
- Example: A rock spontaneously lifting itself off the ground would conserve energy, but it doesn't happen.
- **No Efficiency Limits:** It doesn't explain why heat engines can't convert all heat into work.
- **Need for a New Concept:** This led to the development of the Second Law and the concept of entropy

Entropy (ΔS): A Measure of Disorder

- **Definition:** Entropy (S) is a thermodynamic property that measures the degree of randomness or disorder within a system.
- **Spontaneous Processes:** Natural processes tend to move towards states of higher entropy (greater disorder).
- Example: A dropped glass shatters into many pieces (higher entropy).
- **Statistical Interpretation:** Entropy is related to the number of possible microscopic arrangements (microstates) that correspond to a given macroscopic state. More microstates = higher entropy.
- **Change in Entropy (ΔS):** For a reversible process, $\Delta S = Q_{rev}/T$, where Q_{rev} is the heat transferred reversibly and T is the absolute temperature

Clausius Statement of Second Law

- **Statement:** It is impossible to construct a device which operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.
- **Simple Terms:** Heat cannot spontaneously flow from a colder object to a hotter object without external work being done.
- **Everyday Observation:** This matches our experience – your hot coffee cools down, it doesn't spontaneously get hotter by absorbing heat from the room.
- **Refrigerators:** To make heat flow from cold to hot (like inside a refrigerator), we must put in work (e.g., electricity).

Kelvin-Planck Statement of Second Law

- **Statement:** It is impossible for any device that operates on a cycle to receive heat from a single temperature reservoir and produce a net amount of work.
- **Simple Terms:** You cannot build a heat engine that is 100% efficient in converting heat into work. Some heat must always be rejected to a colder reservoir.
- **Efficiency Limit:** This statement sets the fundamental limit on the efficiency of heat engines.
- **No Perfect Engine:** You cannot get useful work from a heat source unless there's a temperature difference to dump some heat into.

Practical Implications of the Second Law

- **Efficiency Limits:** All real heat engines (like power plants, car engines) and refrigerators have efficiencies less than 100%.
- **Carnot Efficiency:** The theoretical maximum efficiency for any heat engine operating between two temperatures (TH and TC) is given by $\eta carnot=1-TC/TH$. (Temperatures must be in Kelvin).
- **Energy Quality Degradation:** As useful energy is converted, some of it always becomes "unavailable" for doing work (i.e., increases entropy).
- **Heat Transfer Direction:** Explains why heat always flows from hot to cold naturally.
- **Chemical Spontaneity:** Helps predict if chemical reactions will proceed on their own.

Introducing the Third Law of Thermodynamics

- **Focus:** Deals with the behavior of systems as they approach absolute zero temperature.
- **Complementary to Second Law:** Provides a reference point for entropy.
- **Theoretical Limit:** Absolute zero is a theoretical temperature where all thermal motion ceases.

What is Absolute Zero?

- **Definition:** The lowest possible temperature, where particles possess the minimum possible energy.
- **Value:** 0 Kelvin (K), which is equivalent to −273.15 degrees Celsius (∘C) or −459.67 degrees Fahrenheit (∘F).
- **No Molecular Motion:** At absolute zero, all classical translational, rotational, and vibrational motion of atoms and molecules ceases. Only quantum mechanical zero-point energy remains.
- **Unattainable:** The Third Law implies that absolute zero can never be perfectly reached, only approached asymptotically.

Third Law Explained: Entropy at Absolute Zero

- **Statement:** The entropy of a perfect crystalline substance is zero at absolute zero temperature (0 Kelvin).
- **Perfect Crystal:** Implies a perfectly ordered structure with only one possible microstate.
- **Zero Disorder:** At 0K, there's no thermal motion, and if the substance is perfectly ordered, there's no randomness, thus zero entropy.
- **Reference Point:** This law provides an absolute reference point for determining the entropy of a substance at any other temperature.
- **Implication for Reaching Absolute Zero:** Since reaching 0K would require an infinite number of steps to remove all disorder, it's practically impossible.

Summary of All Four Laws

- **Zeroth Law:** Defines temperature; if A is in thermal equilibrium with C, and B is in thermal equilibrium with C, then A and B are in thermal equilibrium.
- **First Law:** Conservation of Energy; Energy cannot be created or destroyed, only transformed ($\Delta U = Q - W$).
- **Second Law:** Direction of Processes; The total entropy of an isolated system (or the universe) never decreases over time. Natural processes increase disorder. Heat engines cannot be 100% efficient.
- **Third Law:** Absolute Zero; The entropy of a perfect crystal at absolute zero temperature is zero. Absolute zero is unattainable.

Thank you

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