UNIT-II
SECOND LAW OF THERMODYNAMICS & AVAILABILITY

G. Anitha | Assistant Professor, Mechanical Department

THERMODYNAMICS

LIMITATIONS OF THE FIRST LAW

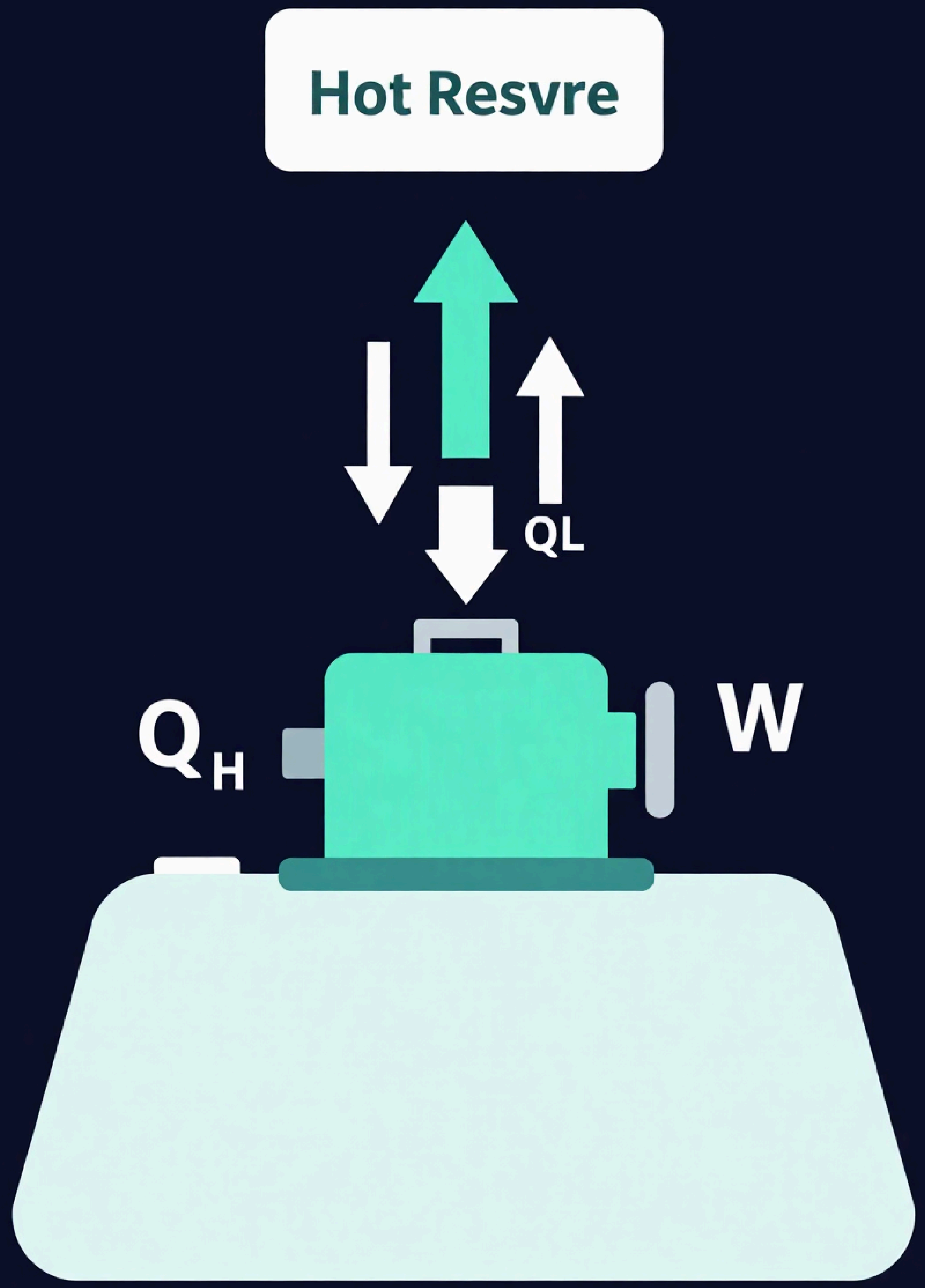
Why the First Law is Insufficient

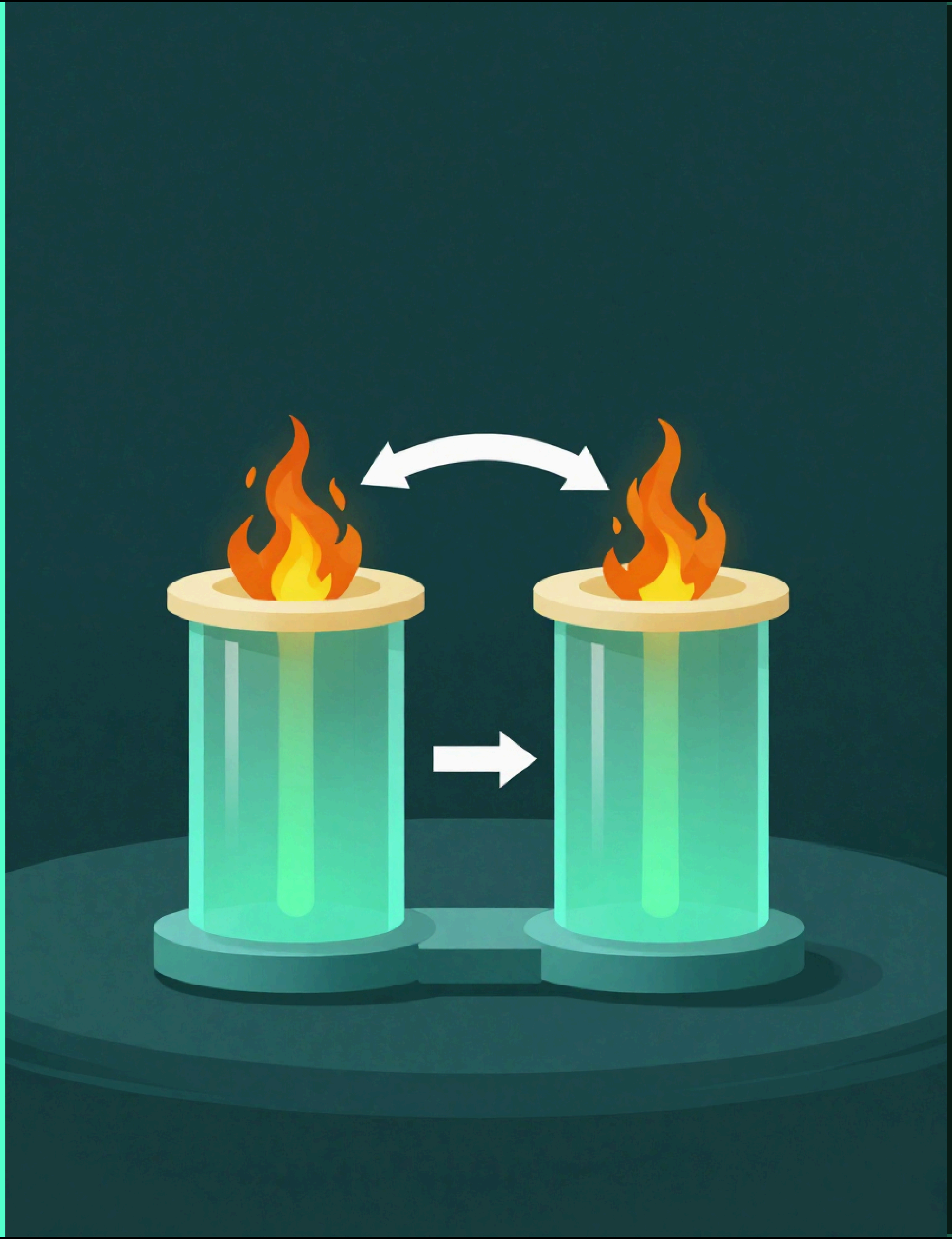
The First Law of Thermodynamics governs energy conservation but fails to predict the direction of processes. It cannot distinguish between spontaneous and non-spontaneous processes, does not account for the quality or grade of energy, and permits theoretically reversible processes that never occur in nature. It gives no information about the feasibility of a process or the maximum work obtainable. These limitations necessitate the Second Law of Thermodynamics.

THERMAL RESERVOIR, HEAT ENGINE & HEAT PUMP

Definitions, Working Principles & Parameters of Performance

Thermal Reservoir: A body with large heat capacity that supplies or absorbs heat without change in temperature. Heat Engine: A device operating in a cycle, converting heat into work — Thermal Efficiency η = W_net / Q_H. Heat Pump: Transfers heat from low to high temperature reservoir using work input. COP (Heat Pump) = Q_H / W. Refrigerator: COP = Q_L / W. Both devices are governed by the Second Law of Thermodynamics and operate between two thermal reservoirs.





SECOND LAW OF THERMODYNAMICS

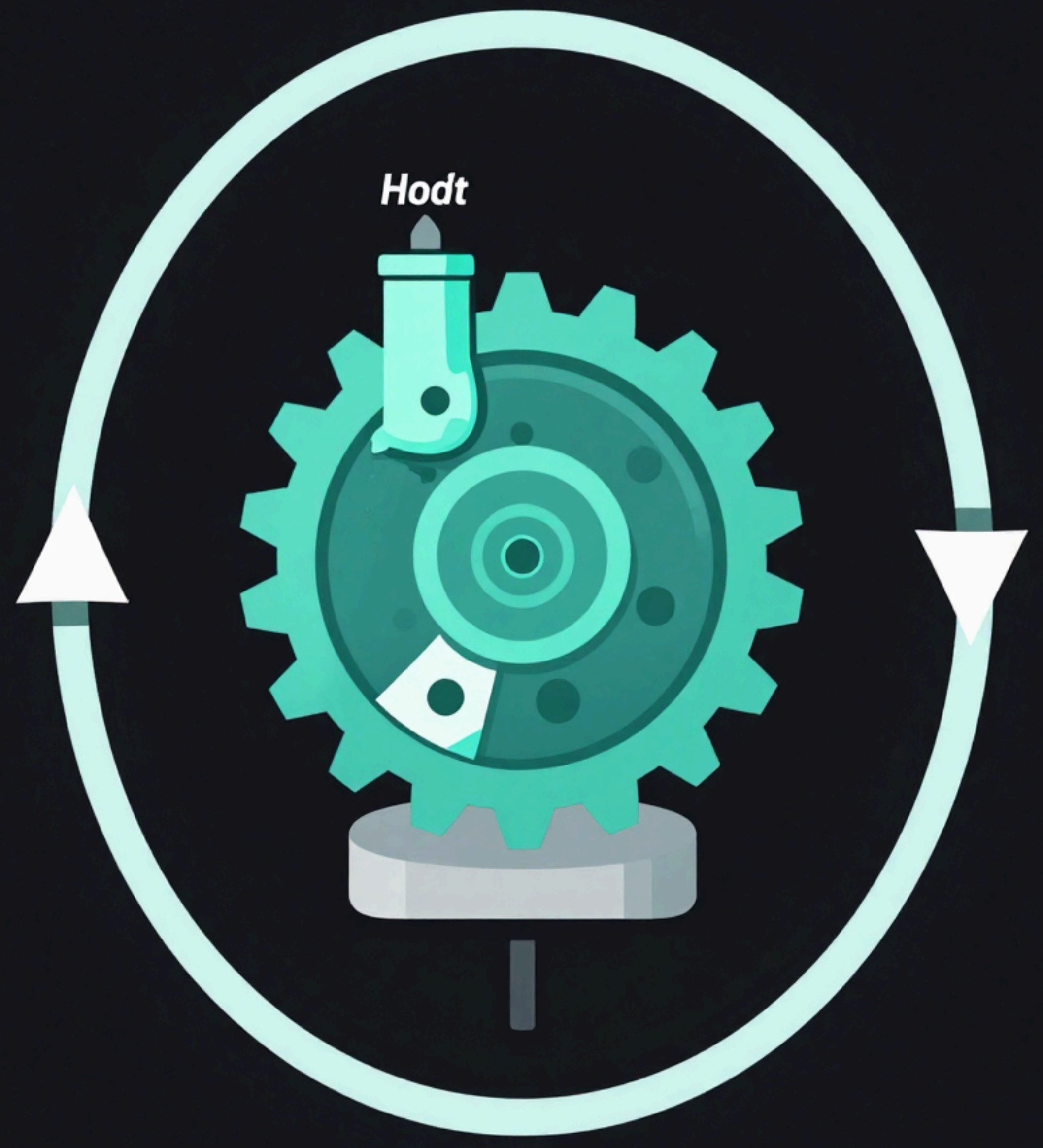
Key Statements & Their Equivalence

Kelvin-Planck Statement: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a single body to produce work.
Clausius Statement: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.
Equivalence: Both statements are equivalent — violation of one implies violation of the other, establishing the foundation of the Second Law.

COROLLARIES & PMM OF SECOND KIND

Impossibility of Perpetual Motion

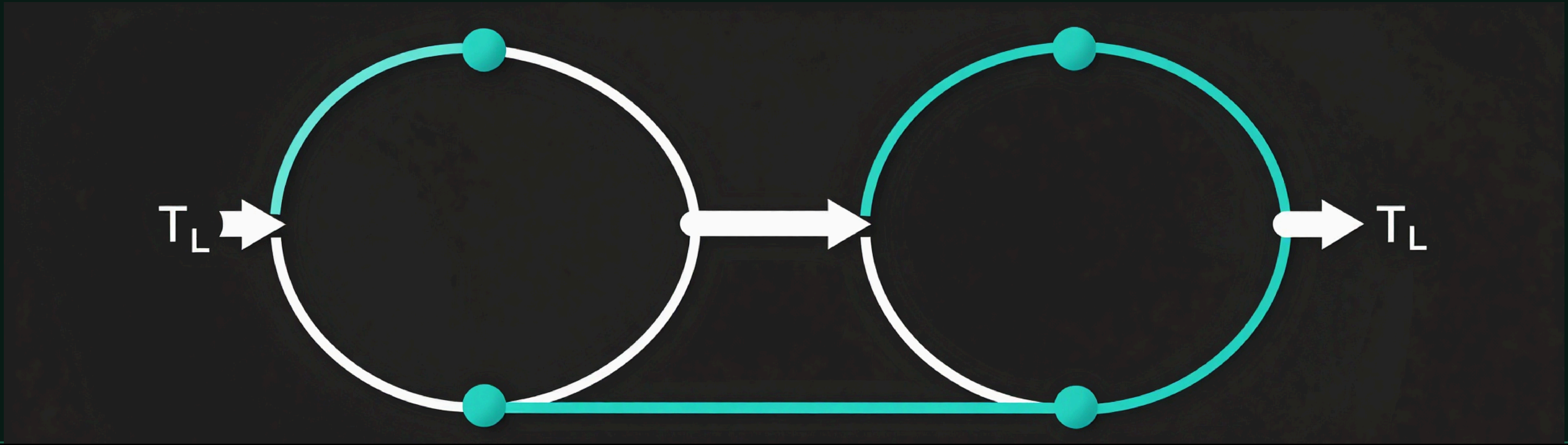
Corollaries of the Second Law: No heat engine can be more efficient than a Carnot engine operating between the same reservoirs. All reversible engines operating between the same two temperatures have equal efficiency. PMM of Second Kind (PMM2): A machine that operates in a cycle, exchanging heat with a single thermal reservoir and producing equivalent work, is impossible. Such a device would violate the Kelvin-Planck statement. Practical Implication: Real engines always have irreversibilities, making their efficiency less than the Carnot (ideal) efficiency. These corollaries set fundamental limits on energy conversion.



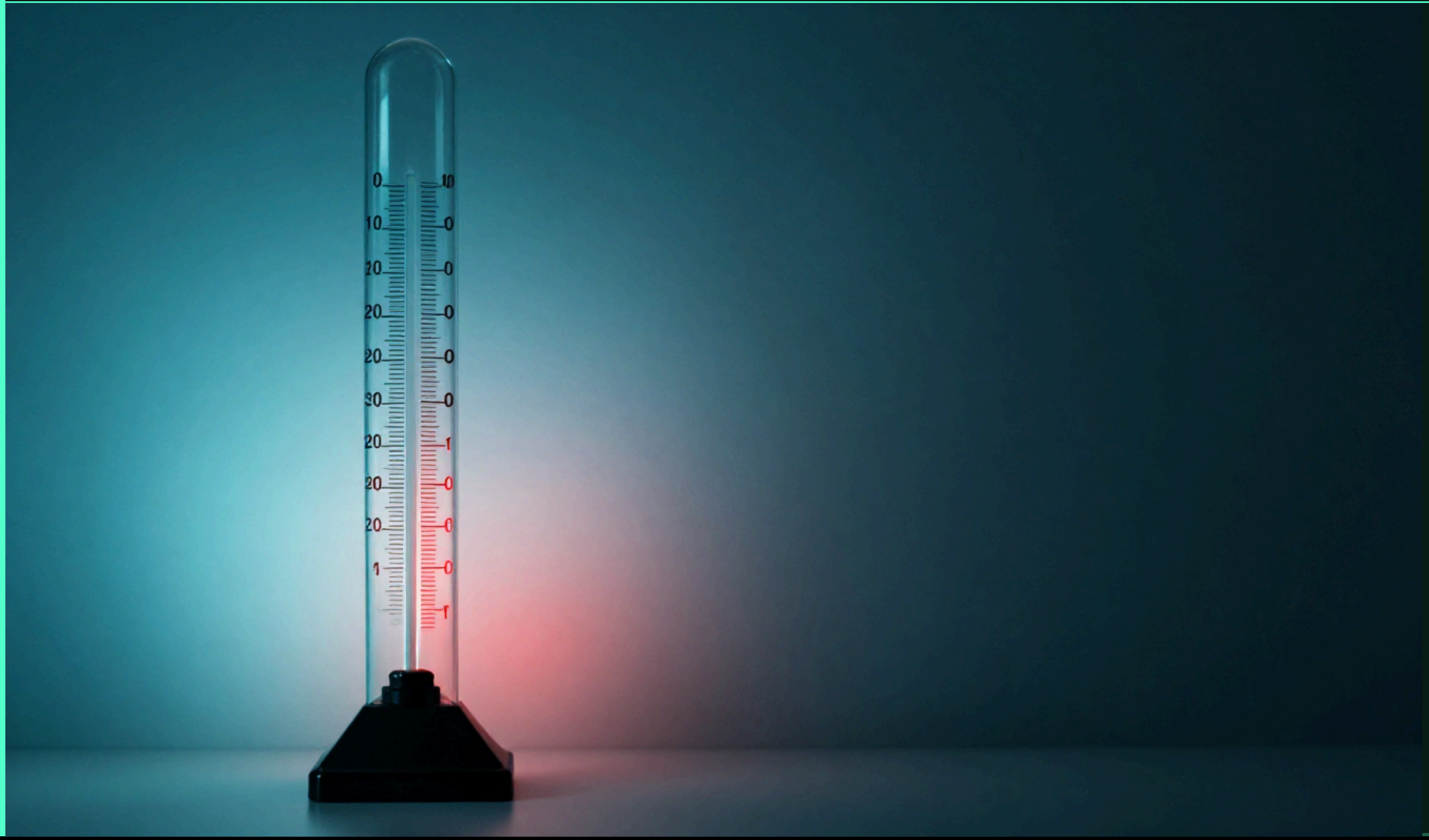
CARNOT'S PRINCIPLE & CARNOT CYCLE

The Foundation of Maximum Efficiency

Carnot's Principle: No heat engine operating between two fixed temperature reservoirs can be more efficient than a reversible (Carnot) engine. The Carnot Cycle consists of four reversible processes: Isothermal Heat Addition, Adiabatic Expansion, Isothermal Heat Rejection, and Adiabatic Compression. Carnot Efficiency: $\eta = 1 - (T_L / T_H)$. The cycle sets the upper bound for all real heat engines and depends solely on source and sink temperatures.



THERMODYNAMIC SCALE OF TEMPERATURE



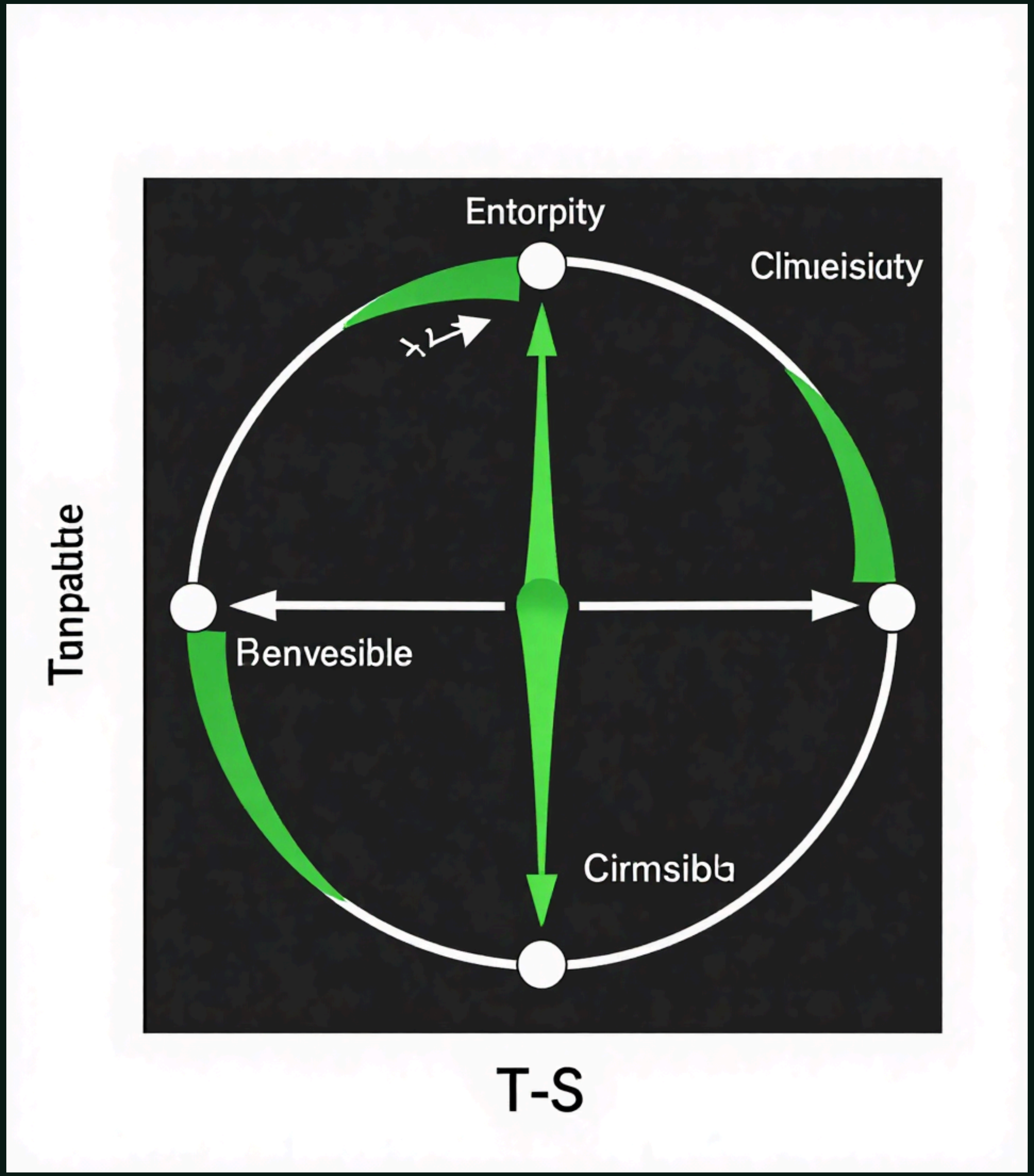
Absolute Temperature & Kelvin Scale

The thermodynamic temperature scale is derived from the Carnot cycle, independent of any working substance. For two heat reservoirs at temperatures T_1 and T_2, the Carnot efficiency defines: $T_2/T_1 = Q_2/Q_1$. The Kelvin scale sets absolute zero (0 K) as the lowest possible temperature, where all molecular motion ceases. The triple point of water (273.16 K) serves as the fixed reference point, establishing a universal, absolute temperature scale.

CLAUSIUS INEQUALITY & ENTROPY

Principle of Entropy Increase & Energy Equation

Clausius Inequality: $\oint(dQ/T) \leq 0$. Entropy (S) is a state property defined as $dS = dQ/T$ (reversible). For irreversible processes, $dS > dQ/T$. Principle of Entropy Increase: The entropy of an isolated system always increases or remains constant — never decreases. Energy Equation: $dU = TdS - PdV$. Entropy generation quantifies irreversibility in real thermodynamic processes.



AVAILABILITY AND IRREVERSIBILITY

Available Energy & Practical Applications

Availability (Exergy) defines the maximum useful work obtainable from a system interacting with the environment. Irreversibility ($I = W_{rev} - W_{actual}$) quantifies lost work due to irreversible processes. Dead state is the condition where system is in equilibrium with surroundings. Higher irreversibility means greater energy degradation. Minimizing irreversibility improves thermodynamic efficiency in real engineering systems such as turbines, compressors, and heat exchangers.

THERMODYNAMIC POTENTIALS

Gibbs Function: $G = H - TS$ | Helmholtz Function: $A = U - TS$ | Used in phase equilibrium, chemical reactions & engineering analysis

THANK YOU!

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