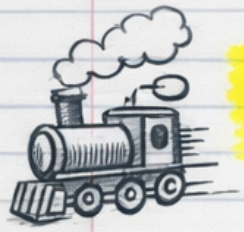
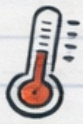
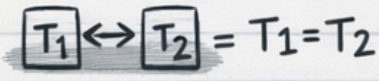
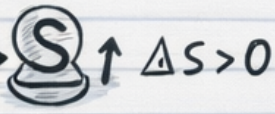


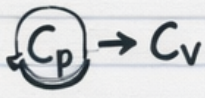
Thermodynamics-I Notes

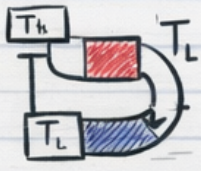
by pyqfort.com

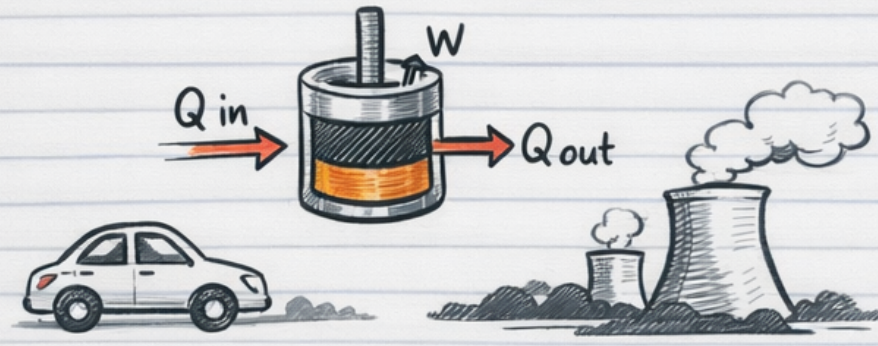
Contents Covered:

- Basic Concepts of Thermodynamics 
- Zeroth Law of Thermodynamics 

- First Law of Thermodynamics $\Delta Q = \Delta U + \Delta W$
- Second Law of Thermodynamics → 

- Concept of Entropy 
- Enthalpy & Specific Heats 

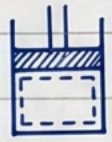
- Carnot Cycle & Efficiency 

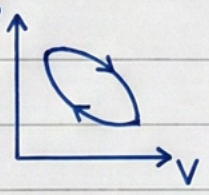


First Law of Thermodynamics (Joule's Law)

Principle: Law of Conservation of Energy

$$\oint \delta Q = \oint \delta W \quad \text{or} \quad \Sigma Q = \Sigma W$$



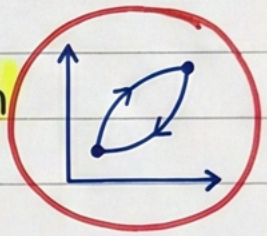


For a Closed System Undergoing a Cycle

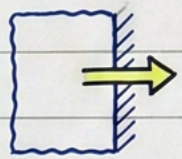
Net heat transfer = Net work transfer.

(Valid for both reversible & irreversible cycles)

Consequence I: Heat Transfer is a Path Function



Type:	Path Function
Nature:	Not a Property
Differential:	Inexact Differential (δ or ∂)
Phenomenon:	Boundary Phenomenon



Consequence II: Energy is a Property

$$\delta Q - \delta W = dE$$
$$\delta Q = dE + \delta W$$

Difference between δQ & δW is constant for any path, hence a Property (Energy).

δQ, δW: Inexact differentials.

dE: Exact differential.

(Valid for Closed System, ANY process)

Special Case: Reversible Process

$$\delta W = P\,dV \qquad \delta Q = dE + P\,dV$$

Valid for Closed System, Reversible Process only.

→ slowly moving piston

Consequence III: Components of Energy (E)

$$E = KE + PE + U$$

KE + PE: Macroscopic energy; U: Microscopic energy

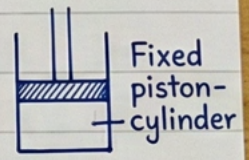
$$dE = d(KE) + d(PE) + dU$$

Simplified First Law Equation

Stationary System: Changes in KE & PE are negligible ($d(KE) \approx 0$, $d(PE) \approx 0$)

$$\Rightarrow \delta Q = dU + \delta W$$

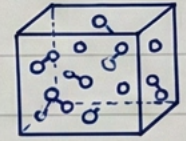
1. Closed System, 2. Rev/Irrev process, 3. Stationary System



Concept: Internal Energy (U): Energy associated with molecular structure/activity

Extensive Property (depends on mass), Unit: kJ

Specific Internal Energy (u): $u = U/m$, Intensive Property (indep. of mass), Unit: kJ/kg

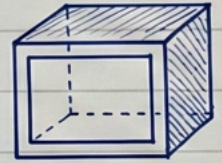


Consequence IV: Energy of an Isolated System

Isolated System: No interaction with surroundings ($\delta Q = 0$, $\delta W = 0$)

$$\delta Q = dE + \delta W \rightarrow 0 = dE + 0 \rightarrow dE = 0 \Rightarrow E_2 = E_1 = \text{Constant}$$

Energy remains constant (Conservation of Energy)



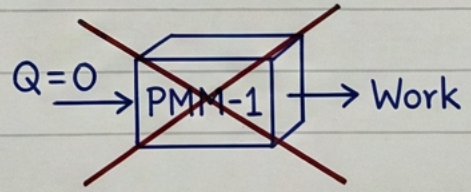
Perfectly insulated rigid box

Consequence V: PMM-1 is Impossible

PMM-1 (Perpetual Motion Machine...): Device to produce work continuously without absorbing energy

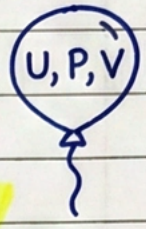
Violates First Law (Conservation of Energy)

Proof: $\oint \delta Q = \oint \delta W \quad (Q = 0 \rightarrow W = 0)$



Thermodynamics: Enthalpy & Specific Heats

1. Enthalpy (H)

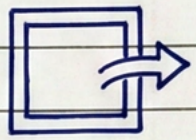


$$H = U + PV$$

Extensive Property — unit: kJ

Intensive Property — $h = \frac{H}{m}$, unit: $\frac{kJ}{kg}$

2. Heat Transfer (Non-Flow)

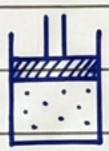


Const. Vol. (V=C): $\delta Q_v = dU$

Internal Energy

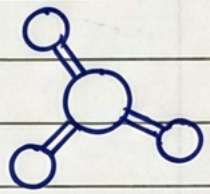
Const. Pres. (P=C): $\delta Q_p = dH$

Enthalpy



3. Ideal Gas Relations

$$dU = mC_v\Delta T$$
$$dH = mC_p\Delta T$$

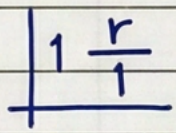


Mayer's Relation: $C_p - C_v = R$

4. Specific Heat Ratios

$\gamma = \frac{C_p}{C_v}$, Adiabatic Index

$C_v = \frac{R}{\gamma - 1}$, $C_p = \frac{\gamma R}{\gamma - 1}$



5. Important Constants (Air)

$C_p = 1.005$	$C_v = 0.718$	$R = 0.287$	$\gamma = 1.4$

Monoatomic gas: $\gamma \approx 1.67$

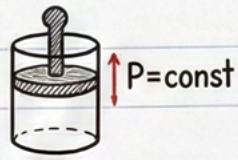
Diatomic gas: $\gamma = 1.4$

Heat Transfer in Non-Flow Processes (Closed System)

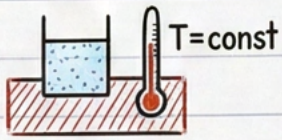
1. Simple Processes (First Law: $\delta Q = dU + \delta W$)

- Isochoric ($V = C$, $\delta W = 0$): $\boxed{\delta Q_v = dU}$

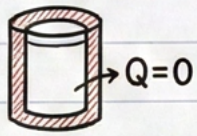
- Isobaric ($P = C$): $\delta Q_p = dU + PdV \Rightarrow \boxed{\delta Q_p = dH}$



- Isothermal ($T = C$, Ideal Gas $\Rightarrow dU = 0$): $\boxed{\delta Q = \delta W}$



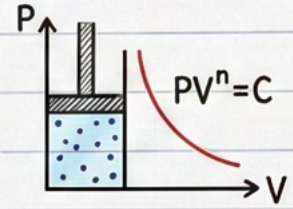
- Adiabatic (No Heat): $\boxed{\delta Q = 0}$



2. Polytropic Process ($PV^n = C$)

$$\delta Q_{poly} = dU + \delta W_{poly}$$
$$= mC_v\,dT + \frac{P_1V_1 - P_2V_2}{n-1}$$
$$= m\left(\frac{R}{\gamma-1}\right)(T_2 - T_1) + \ldots$$

(derivation steps omitted for brevity)



$$\boxed{\delta Q_{poly} = \left(\frac{\gamma - n}{\gamma - 1}\right) \times \delta W_{poly}}$$

3. Polytropic Specific Heat (C_{poly})

Analogy: $\delta Q = m\,C\,dT$. Also, $\delta Q_{poly} = \frac{\gamma - n}{\gamma - 1} \cdot \left[\frac{mR\,dT}{n-1}\right]$

Equating them and simplifying (with $R/C_v = \gamma - 1$): $\boxed{C_{poly} = \left(\frac{n - \gamma}{n - 1}\right) \times C_v}$

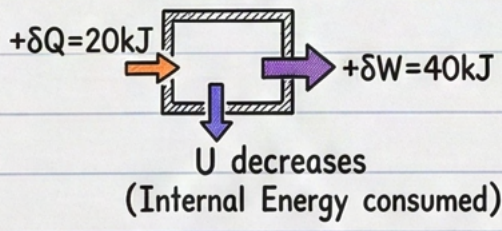
4. Conceptual Analysis: Why is C_{poly} Negative?

Usually, $1 < n < \gamma$ (e.g., $n = 1.2$, $\gamma = 1.4$) [C_{poly} is Negative]

Example: $\delta Q_{poly} = \left(\frac{1.4 - 1.2}{1.4 - 1}\right) \delta W_{poly} = 0.5\,\delta W_{poly} \Rightarrow \boxed{\delta W_{poly} = 2 \times \delta Q_{poly}}$

Reasoning: If Heat Supplied ($\delta Q = +20$ kJ), Work Done ($\delta W = +40$ kJ).

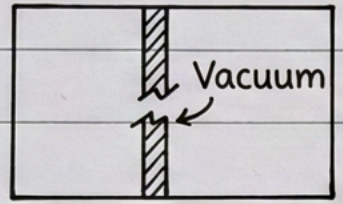
Work Done > Heat Supplied!



Extra work comes from Internal Energy (U).
So, U decreases → Temperature (T) decreases.
[Though heat is added, T drops!]

Summary: In a polytropic process, heat transfer is a fraction of work transfer, and specific heat is derived from this relation, often being negative for common n values.

Free Expansion: Expansion against vacuum is called free expansion. Here, $dQ = 0$ and $dW = 0$. But $PdV \neq 0$, so $PdV \neq dW$ (irreversible process).

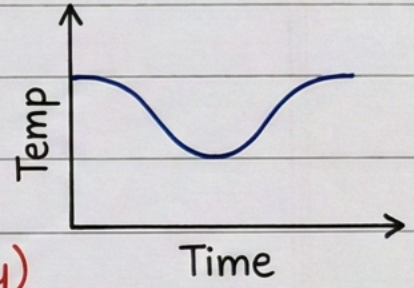


$dU = dQ - dW = 0 \Rightarrow U_f = U_i$ (for any gas).

$U_f = U_i$

For ideal gas, $dU = nC_v\,dT = 0 \Rightarrow T_f = T_i$

Since $H = U + PV = f(T)$ for ideal gas, $H_f = H_i$ (for ideal gas only)



Process is not isothermal.

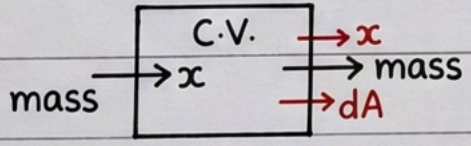
Adiabatic Process (Reversible): $dQ = 0$. $dQ = dU + dW$. $0 = nC_v\,dT + PdV$

also $H = U + PV$, $dH = dU + PdV + VdP$, $nC_p\,dT = VdP$

$$\frac{VdP}{PdV} = -\frac{nC_p\,dT}{nC_v\,dT} = -\gamma \cdot \int \frac{dV}{V} = -\gamma \int \frac{dP}{P} \Rightarrow \ln V = -\gamma \ln P + C \Rightarrow \ln(PV^{\gamma}) = C \Rightarrow \boxed{PV^{\gamma} = \text{Constant}}$$

*Valid for reversible adiabatic process of ideal gas.

Displacement Work: Work done by mass entering or leaving a control volume (C.V.).



$W = PdV \Rightarrow W_{flow} = PV.$

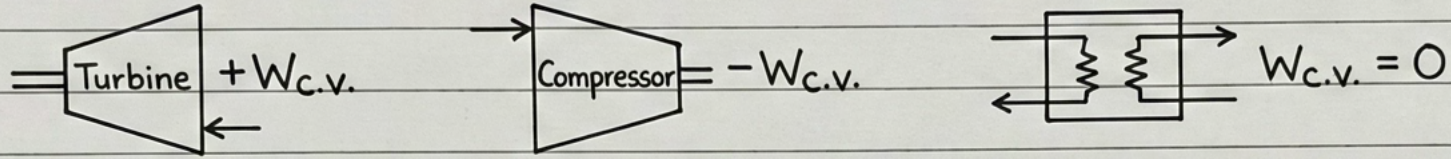
Entry work $= -P_1V_1$, Exit work $= P_2V_2$

Open System Analysis (SFEE)

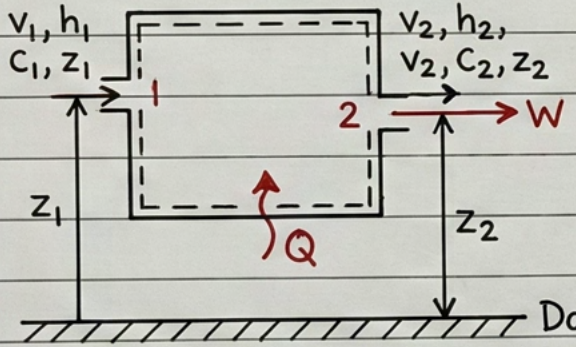
SFEE = Steady Flow Energy Equation

Assumptions : 'Steady flow' $\Rightarrow (\text{mass entering})_{CV} = (\text{mass leaving})_{CV}$

Principle : Energy entering C.V. = Energy leaving C.V.



W = Entry disp. work + $W_{c.v.}$ + Exit disp. work $\Rightarrow W = -P_1V_1 + W_{c.v.} + P_2V_2$ --- (1)



Energy entering = Energy leaving $\Rightarrow$

$$\frac{1}{2}mC_1^2 + mgz_1 + U_1 + Q = \frac{1}{2}mC_2^2 + mgz_2 + U_2 + W$$

$$\frac{1}{2}mC_1^2 + mgz_1 + U_1 + Q = \frac{1}{2}mC_2^2 + mgz_2 + U_2 + [-P_1V_1 + W_{c.v.} + P_2V_2]$$

$$\frac{1}{2}mC_1^2 + mgz_1 + U_1 + P_1V_1 + Q = \frac{1}{2}mC_2^2 + mgz_2 + U_2 + P_2V_2 + W_{c.v.}$$

Since $H = U + PV$

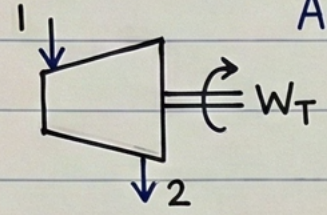
$$\frac{1}{2}mC_1^2 + mgz_1 + H_1 + Q = \frac{1}{2}mC_2^2 + mgz_2 + H_2 + W_{c.v.}$$

Divide both sides by 'm' :

$$\boxed{\frac{1}{2}C_1^2 + gz_1 + h_1 + q = \frac{1}{2}C_2^2 + gz_2 + h_2 + \omega_{c.v.}}$$ SFEE

First law of thermodynamics for open systems

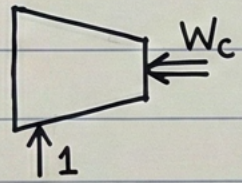
Turbine: Work done by the system.



Assumptions: 1) Steady flow
2) Perfectly insulated ($q=0$)
3) KE changes are negligible ($c_1 \approx c_2$)
4) PE changes are negligible ($z_1 \approx z_2$).

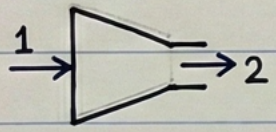
SFEE: $h_1 = h_2 + W_{cv} \Rightarrow \boxed{W_T = h_1 - h_2}$

Compressor: Work done on the system.



$W_{cv} = h_1 - h_2 \Rightarrow -W_{comp} = h_1 - h_2 \Rightarrow \boxed{W_{comp} = h_2 - h_1}$

Nozzle: Device converts pressure energy into kinetic energy. No work transfer.



1) Steady flow 2) PE changes negligible 3) Perfectly insulated ($q=0$)

SFEE: $\boxed{h_1 + \frac{c_1^2}{2} = h_2 + \frac{c_2^2}{2}}$ * if $c_2 \gg c_1$, $h_1 = h_2 + \frac{c_2^2}{2}$

Throttling: Porous plug, partially opened valve, orifice.

1) No heat transfer ($dq=0$, $q=0$) 2) No work transfer ($dw=0$, $W_{cv}=0$)
3) Highly irreversible process 4) Isenthalpic process.

SFEE: $\boxed{h_1 = h_2}$ ~~isenthalpic~~ process (PE & KE changes negligible)

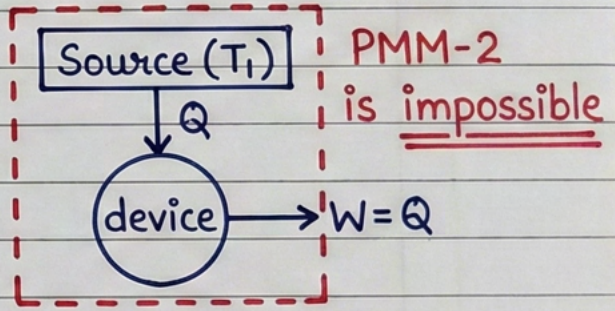
TER (Thermal Energy Reservoir)

1) Source: It supply large amount of thermal energy without undergoing any temperature change within it.
2) Sink: It has capacity to absorb large amount of thermal energy without undergoing any temperature change within it.

Note: Work is a high grade energy and heat is a low grade energy. Complete conversion of low grade energy (Heat) into high grade energy (work) is impossible in a cycle.

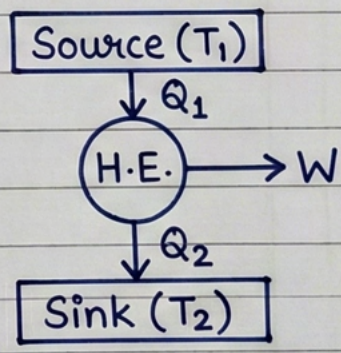
Kelvin-Planck Statement

It is impossible to develope a device operating in a cycle which produces work continuously by exchanging heat with a single reservoir.



Heat Engine

It is a device which converts part of heat supplied in work and rejects remaining heat to sink.



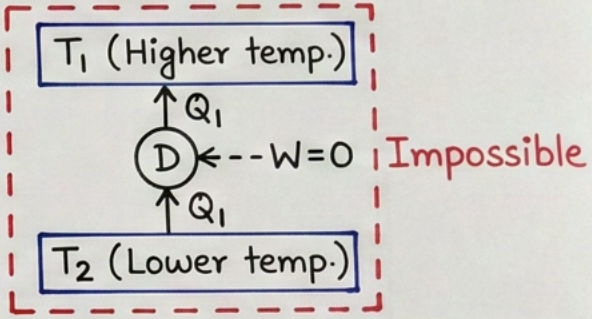
$$\text{Efficiency} = \frac{\text{Output}}{\text{Input}}, \quad \eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = 1 - \left(\frac{Q_2}{Q_1}\right)$$

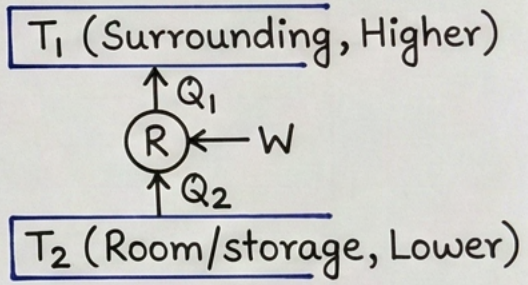
↳ Valid for rev. or irr. engine

Clausius Statement

It is impossible to develop a device operating in a cycle which transfer heat from lower temp. to higher temp. without any external aid.



Refrigerator: It maintains lower temp. compare to surrounding while operating in a cycle.

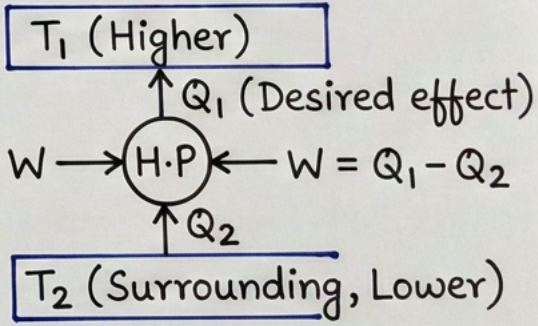


COP (Coefficient of Performance)

$$COP_R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

$$\boxed{COP_R = \frac{Q_L}{Q_H - Q_L}} \rightarrow \text{Valid for rev. or irr. cycle}$$

Heat Pump: It maintains higher temperature compare to surrounding while operating on a cycle.

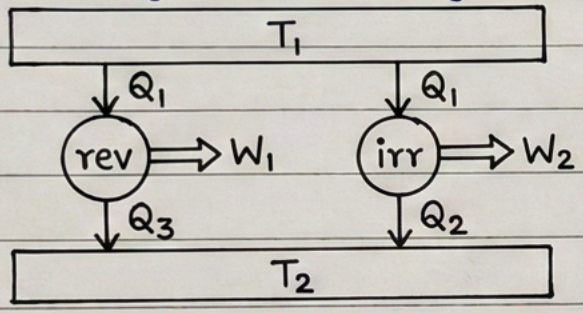


$$COP_{HP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} \quad ; \quad \boxed{COP_{HP} = \frac{Q_H}{Q_H - Q_L}}$$

$$\boxed{COP_{HP} - COP_R = 1} \rightarrow \text{Relation b/w COP of H·P and Refrigerator operating b/w same temp limits}$$

Carnot's Theorem

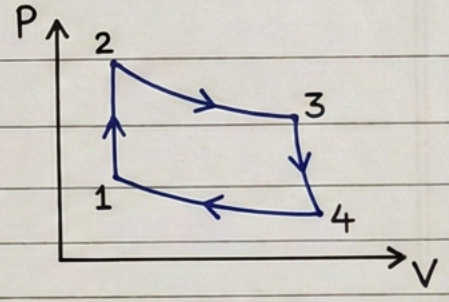
It states that for all engines working between the same temperature limits, reversible cycle efficiency is greater than irreversible cycle efficiency.



$$\eta_{rev} > \eta_{irr}$$

Carnot Cycle (Reversible Cycle)

1-2 → Adiabatic Compression 2-3 → Isothermal Expansion
3-4 → Adiabatic Expansion 4-1 → Isothermal Compression



Carnot cycle consists of two adiabatic and two isothermal processes. To realize isothermal process, piston must move at very slow rate whereas for adiabatic process piston must move at very fast rate, hence these two processes in a cycle are practically impossible. Therefore, Carnot cycle is used for comparison.

Note → Efficiency of reversible cycle depends only on temperature limits and all reversible engines working between same temperature limits have same efficiency. That is η_{rev} is independent of working fluid (fuel) and depends only on temperature limits.

From Carnot efficiency (η) equations:

$$\eta_1 = 1 - \frac{Q_2}{Q_1} = f_1(T_1, T_2)\ ;\ \eta_2 = 1 - \frac{Q_3}{Q_2} = f_2(T_2, T_3)\ ;\ \eta_3 = 1 - \frac{Q_3}{Q_1} = f_3(T_1, T_3)$$

$$\Rightarrow \frac{Q_1}{Q_2} = \frac{1}{[1 - f_1(T_1, T_2)]} = \phi_1(T_1, T_2)$$

$$\frac{Q_2}{Q_3} = \phi_2(T_2, T_3)$$

$$\phi_1(T_1, T_2) = \left[\frac{Q_1/Q_3}{Q_2/Q_3}\right] = \frac{\phi_3(T_1, T_3)}{\phi_2(T_2, T_3)}$$

Since T_3 is constant, we define a function $\Psi(T)$ such that $\phi(T_a, T_b) = \frac{\Psi(T_a)}{\Psi(T_b)} = \frac{T_a}{T_b}$

$$\boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$$ (for reversible cycle only)

Kelvin Scale definition using Triple Point (T.P.) of water

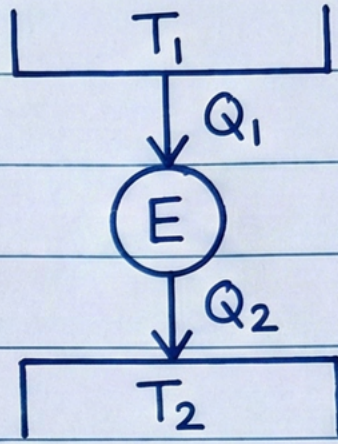
T.P. = 0·01 °C = 273·16 K

$$\boxed{T = 273{\cdot}16 \times \frac{Q}{Q_{tp}}}$$

Here, heat (Q) is used as a thermometric property.

Efficiency of reversible engine

$$\eta = 1 - \frac{Q_2}{Q_1}$$



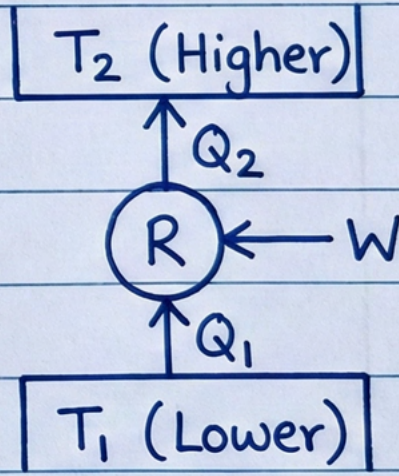
From Carnot's theorem, $Q_1/Q_2 = T_1/T_2$

$$\eta_{rev} = 1 - \frac{T_2}{T_1} = 1 - \frac{T_L}{T_H}$$

(for reversible process only)

COP of reversible refrigerator

$$COP = \frac{Q_1}{Q_2 - Q_1}, \quad COP = \frac{1}{Q_2/Q_1 - 1}$$

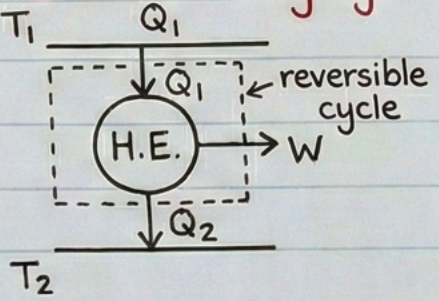


$$COP_{rev} = \frac{1}{T_2/T_1 - 1} = \frac{T_1}{T_2 - T_1}$$

$$COP_{rev} = \frac{T_L}{T_H - T_L}$$

Clausius Inequalities

Definition: The cyclic integral of $\frac{\delta Q}{T}$ is ≤ 0 for any cycle.



Case I: Reversible cycle

For a reversible cycle operating between T_1 and T_2: $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

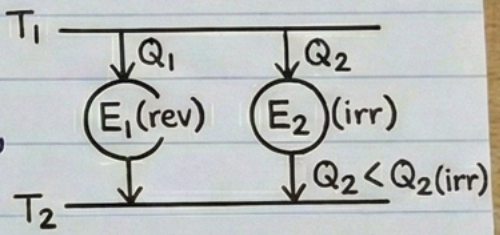
The cyclic integral is: $\oint\left(\frac{\delta Q}{T}\right) = +\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$. $\boxed{\oint\left(\frac{\delta Q}{T}\right) = 0}$

Case II: Irreversible Cycle

We know that $\eta_{rev} > \eta_{irr}$. Therefore, $W_{rev} > W_{irr} \Rightarrow$

$(Q_1 - Q_2) > (Q_1 - Q_{2irr}) \Rightarrow Q_2 < Q_{2irr}$

Now, $\oint_{irr}\left(\frac{\delta Q}{T}\right) = \frac{Q_1}{T_1} - \frac{Q_{2irr}}{T_2}$. Since $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ (for rev) and $Q_2 < Q_{2irr}$, then the term $\frac{Q_{2irr}}{T_2}$ is larger than $\frac{Q_1}{T_1}$. Thus, $\boxed{\oint_{irr}\left(\frac{\delta Q}{T}\right) < 0}$

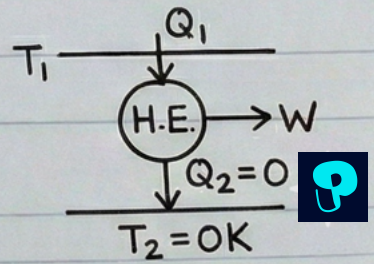


Third Law of Thermodynamics:

It is impossible by any procedure to reduce any system to absolute zero Kelvin temperature in a finite number of operations.

PPM-3:

A machine which in continuous motion is complete absence of friction is PMM 3 and it is impossible.



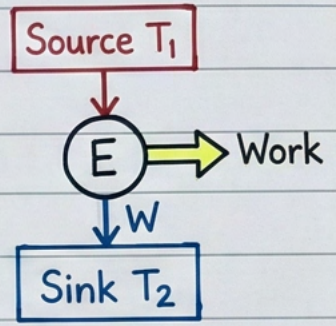
Topic: Proof of Unattainability of Absolute Zero (0 K)

Objective: To prove that reaching Absolute Zero (0 K) is thermodynamically impossible using the Second Law of Thermodynamics.

1. Mathematical Premise: For a reversible heat engine (Carnot engine) between source (T_1) and sink (T_2), $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

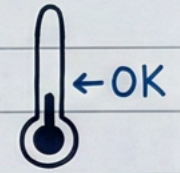
   Where: Q_1 = Heat supplied, T_1 = Source temp, Q_2 = Heat rejected, T_2 = Sink temp

   Rearranging for Heat Rejected (Q_2): $Q_2 = T_2 \times (Q_1/T_1)$



2. The Assumption (Proof by Contradiction): Assume it IS possible to reach Absolute Zero at the sink.

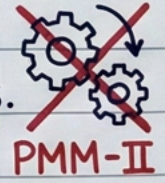
   Assumption: $T_2 = 0$ K. Substituting: $Q_2 = 0 \times (Q_1/T_1) \rightarrow Q_2 = 0$



3. The Implication: If $Q_2 = 0$, engine rejects NO heat to the sink. Engine converts entire Q_1 into Work (W). $W_{net} = Q_1 - Q_2 \rightarrow W_{net} = Q_1$ (100% Efficiency)

4. The Violation (Conclusion): An engine producing work while exchanging heat with ONLY ONE reservoir ($Q_2 = 0$) is a Perpetual Motion Machine of the Second Kind (PMM-II). This is a direct violation of the Kelvin-Planck Statement of the Second Law of Thermodynamics.

   Final Verdict: Since Kelvin-Planck cannot be violated, the assumption is FALSE. Therefore, Absolute Zero (0 K) is impossible to attain.



Thermodynamics: Mixture of Ideal Gases

1. Basics & Definitions

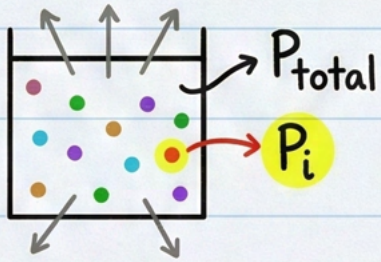
Mole Fraction (χ_i)

↳ Ratio of moles of one gas to total moles

$$\chi_i = n_i / \Sigma n$$

Partial Pressure (P_i)

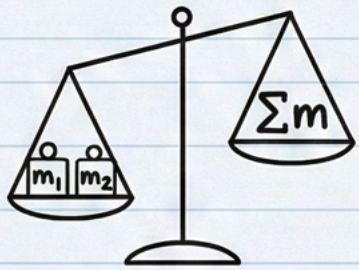
$$P_i = P \cdot \chi_i$$



2. Equivalent Properties (Mixture as one gas)

Equivalent Gas Constant (R_e) MASS-WEIGHTED average

$$R_e = (\Sigma m_i R_i)/(\Sigma m)$$



C_{Pe}, C_{ve}

$$C_{Pe} = \frac{(\Sigma m_i C_{Pi})/(\Sigma m)}{\Sigma m}$$

Equivalent Molecular Weight (M_e) MOLE-WEIGHTED average

$$M_e = \Sigma \chi_i M_i$$

$$\Sigma \chi_i = 1$$

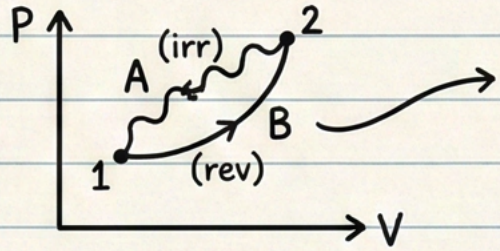
Summary Sheet

Property	Formula	Basis
Mole Fraction	$\chi_i = n_i / \Sigma n$	Moles
Partial Pressure	$P_i = P \cdot \chi_i$	Moles
Equiv. R_e & C_p, C_v	$R_e = \frac{\Sigma m_i R_i}{\Sigma m}$	Mass
Equiv. M_e	$M_e = \Sigma \chi_i M_i$	Moles

ENTROPY (S) & CLAUSIUS INEQUALITY

1. WHAT IS ENTROPY?

Entropy is a **property**, a **point function**. Its value depends ONLY on the end states, NOT the path.

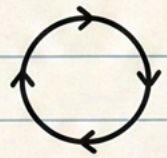


→ ΔS is SAME for both paths if end points are fixed!

2. FOR REVERSIBLE PROCESS

Defined from rev. cycles. The quantity $\int \frac{\delta Q}{T}$ is path-independent.

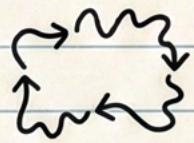
$$dS = \left(\frac{\delta Q}{T}\right)_{rev}$$



3. FOR IRREVERSIBLE PROCESS

From Clausius Inequality ($\oint \frac{\delta Q}{T} < 0$ for irr. cycle), we derive:

$$dS > \left(\frac{\delta Q}{T}\right)_{irr}$$



* To find ΔS for irr. process, replace it with a **REVERSIBLE path** between same end points & calculate $\int \left(\frac{\delta Q}{T}\right)_{rev}$.

4. COMBINED CONDITION (CLAUSIUS)

$$dS \geq \frac{\delta Q}{T}$$

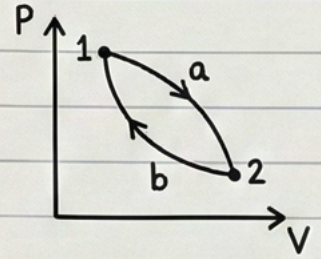
= for **Reversible**
> for **Irreversible**
< is **IMPOSSIBLE**

MATHEMATICAL PROOF: ENTROPY & CLAUSIUS INEQUALITY

1. Reversible Cycle (Clausius Equality)

For any reversible cycle, the cyclic integral of $\frac{\delta Q}{T}$ is zero.

$$\oint \left(\frac{\delta Q}{T}\right)_{rev} = 0$$



Split into paths: $\int \left(\frac{\delta Q}{T}\right)_{1-a-2} + \int \left(\frac{\delta Q}{T}\right)_{2-b-1} = 0$

Rearranging: $\int \left(\frac{\delta Q}{T}\right)_{1-a-2} = -\int \left(\frac{\delta Q}{T}\right)_{2-b-1} = \int \left(\frac{\delta Q}{T}\right)_{1-b-2}$

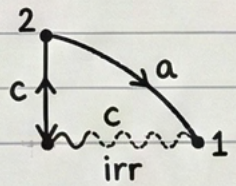
2. Path Independence & Definition of S

Since the integral is the same for paths 'a' and 'b', the quantity $\int \left(\frac{\delta Q}{T}\right)_{rev}$ is independent of the path and depends ONLY on end points.

This defines a Property called Entropy (S). $dS = \left(\frac{\delta Q}{T}\right)_{rev}$

3. Irreversible Cycle (Clausius Inequality)

For a cycle with at least one irreversible process, the cyclic integral is negative. $\oint \left(\frac{\delta Q}{T}\right) < 0$



Consider cycle with rev path 1-a-2 and irr path 2-c-1: $\int \left(\frac{\delta Q}{T}\right)_{1-a-2} + \int \left(\frac{\delta Q}{T}\right)_{2-c-1} (irr) < 0$

4. Deriving the Inequality

Substitute the rev part with dS: $\int dS_{1-2} + \int \left(\frac{\delta Q}{T}\right)_{2-c-1} (irr) < 0$

$$S_2 - S_1 + \int \left(\frac{\delta Q}{T}\right)_{irr} < 0$$

Rearranging for infinitesimal change $\Rightarrow$ $dS > \left(\frac{\delta Q}{T}\right)_{irr} > 0$

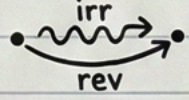
5. Combined Condition & Note

Combining both cases gives the general Clausius Inequality:

$$dS \geq \frac{\delta Q}{T}$$

= for Reversible

> for Irreversible



Important Note: To calculate ΔS for an irreversible process, you MUST use a REVERSIBLE path between the same end states.