

# Second Law of Thermodynamics

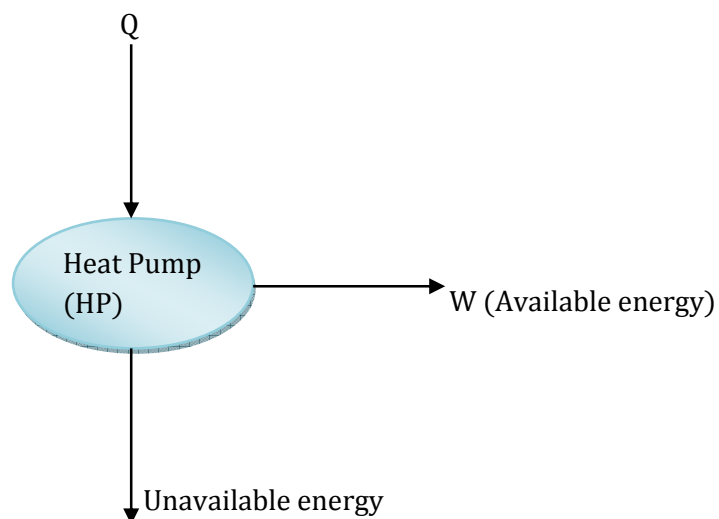
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## Necessity of Formulation of Second Law

- The first law of thermodynamics states that a certain energy balance will hold when a system undergoes a change of state or a thermodynamic process. But it does not give any information on whether the change of state or the process is at all feasible or not.
- The Second Law gives directional possibility of physical phenomena and concept of entropy.

## Entropy

Entropy is the randomness or disorder of a thermodynamics system. It is an extensive property of a system that is used to measure unavailable energy (loss).



Increase in entropy

- ⇒ Increase in randomness
- ⇒ Increase in unavailable energy
- ⇒ Decrease in available energy

Mathematically, change in entropy can be written as

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

> - Irreversible Process (.....)

= - Reversible Process (\_\_\_\_\_)

Entropy Balance Equation can be written as:

$$[\text{Entropy entering into the system}] - [\text{Entropy leaving the system}]$$

+ [Entropy generation of the system] = [Change in entropy of the system]

Hence,  $S_{in} - S_{out} + S_{gen} = \Delta S$

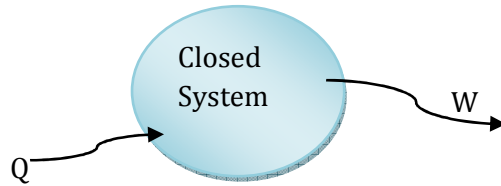
### Isolated System

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$$S_{gen} = \Delta S$$

### Closed System

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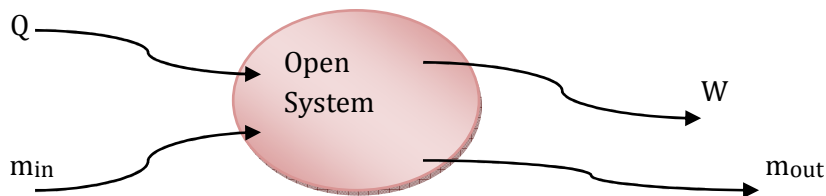
$$\sum \frac{Q}{T}(\text{entering}) - 0 + S(\text{generated}) = \Delta S(\text{control mass})$$

[Since, Work is entropy free energy. So,  $S_{out} = 0$ ]

Hence,  $\sum \frac{Q}{T}(\text{entering}) + S(\text{generated}) = \Delta S(\text{control mass})$

### Open System

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$$\sum \frac{Q}{T}(\text{entering}) + m \cdot s(\text{in}) - m \cdot s(\text{out}) + S(\text{generated}) = \Delta S(\text{control volume})$$

Differentiating both sides w.r.t. time,

$$\sum \frac{\dot{Q}}{T}(\text{entering}) + \dot{m} \cdot s(\text{in}) - \dot{m} \cdot s(\text{out}) + \dot{S}(\text{generated}) = \Delta \dot{S}(\text{control volume})$$

This is the Second Law for Unsteady Flow.

For SSSF,

$$\Delta S(\text{control volume}) = 0$$

$$m_{in} = m_{out} = m(\text{say})$$

Then,

$$\sum \frac{\dot{Q}}{T}(\text{entering}) + \dot{m}[s(\text{in}) - s(\text{out})] + \dot{S}(\text{generated}) = 0$$

## Reversible and Irreversible Processes

### Reversible Process

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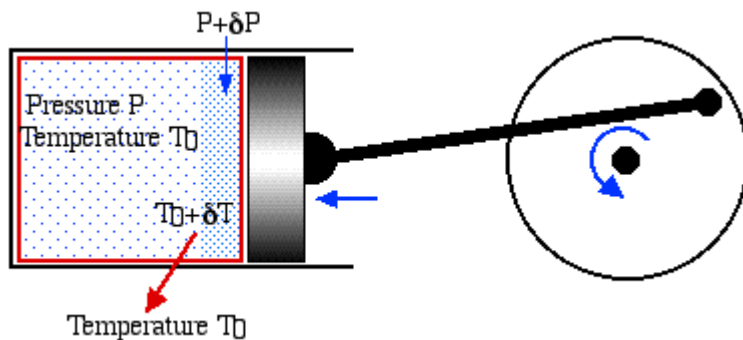
A process is reversible if, after the process has been completed, means can be found to restore the system and all elements of its surroundings to their respective initial states.

### Irreversible Process

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A process is called irreversible if the system and all parts of the surroundings cannot be exactly restored to their respective initial states after the process has occurred.

Consider an example of a reversible piston cylinder device in thermal equilibrium with the surroundings at temperature  $T_0$ , and undergoing a cyclic compression/expansion process.



For mechanical reversibility we assume that the process is frictionless, however we also require that the process is a quasi-equilibrium one. In the diagram we notice that during compression the gas particles closest to the piston will be at a higher pressure than those farther away, thus the piston will be doing more compression work than it would do if we had waited for equilibrium conditions to occur after each incremental step. Similarly, thermal reversibility requires that all heat transfer is isothermal. Thus if there is an incremental rise in temperature due to compression then we need to wait until thermal equilibrium is established. During expansion the incremental fall in temperature will result in heat being transferred *from* the surroundings *to* the system until equilibrium is established.

In summary, there are three conditions required for reversible operation:

- All mechanical processes are frictionless.
- At each incremental step in the process thermal and pressure equilibrium conditions are established.
- All heat transfer processes are isothermal.

## Change in Entropy for Ideal Gas/Perfect Gas/Compressible Substance

Using First Law of Thermodynamics

$$\delta Q - \delta W = dU \dots \dots \dots (i)$$

From definition of entropy for reversible process,

$$dS = \frac{\delta Q}{T} \dots \dots \dots (ii)$$

From (i) and (ii),  $T \cdot dS - \delta W = dU$

$$\text{Or, } T \cdot dS = \delta W + dU$$

$$\text{Or, } T \cdot dS = P \cdot dV + dU \dots \dots \dots (iii)$$

From definition of enthalpy,

$$H = U + PV$$

Differentiating both sides,

$$dH = dU + p \cdot dV + V \cdot dP$$

$$\text{Or, } dH = T \cdot dS + V \cdot dP$$

$$\text{Or, } T \cdot dS = dH - V \cdot dP \dots \dots \dots (iv)$$

From equation (iii),

$$dS = \frac{dU}{T} + \frac{P \cdot dV}{T}$$

$$\text{Or, } dS = \frac{m \cdot C_v \cdot dT}{T} + m \cdot R \cdot \frac{dV}{V} \quad [\text{Since, } PV = mRT]$$

Integrating both sides,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} m \cdot C_v \cdot \frac{dT}{T} + \int_{V_1}^{V_2} m \cdot R \cdot \frac{dV}{V}$$

$$\Rightarrow S_2 - S_1 = m \int_{T_1}^{T_2} C_v \cdot \frac{dT}{T} + mR \log_e \frac{V_2}{V_1}$$

This equation is for variable specific heat capacity.

$$\Rightarrow S_2 - S_1 = m \cdot C_v \cdot \log_e \frac{T_2}{T_1} + mR \log_e \frac{V_2}{V_1}$$

From equation (iv),

$$dS = \frac{dH}{T} - \frac{V \cdot dP}{T}$$

$$\Rightarrow dS = \frac{m \cdot Cp \cdot dT}{T} - m \cdot R \cdot \frac{dP}{P}$$

Integrating both sides,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} m \cdot Cp \cdot \frac{dT}{T} - \int_{P_1}^{P_2} m \cdot R \cdot \frac{dP}{P}$$

$$\Rightarrow S_2 - S_1 = m \int_{T_1}^{T_2} Cp \cdot \frac{dT}{T} - mR \log_e \frac{P_2}{P_1}$$

This equation is for variable specific heat capacity.

$$\Rightarrow S_2 - S_1 = m \cdot Cp \cdot \log_e \frac{T_2}{T_1} - mR \log_e \frac{P_2}{P_1}$$

## Change in Entropy for Adiabatic Process

From definition of entropy,

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

For adiabatic process,  $\delta Q = 0$

Hence,  $dS \geq 0$

For reversible adiabatic process,  $dS = 0$

$\Rightarrow S = \text{constant}$

$\Rightarrow$  Constant entropy/Isentropic process

## Relationship between Temperature, Pressure and Volume for Isentropic Process

Change in entropy for reversible process can be written as:

$$\Rightarrow S_2 - S_1 = m \cdot Cv \cdot \log_e \frac{T_2}{T_1} + mR \log_e \frac{V_2}{V_1} \dots \dots \dots (i)$$

$$\Rightarrow S_2 - S_1 = m \cdot Cp \cdot \log_e \frac{T_2}{T_1} - mR \log_e \frac{P_2}{P_1} \dots \dots \dots (ii)$$

For reversible adiabatic process ( $S_1=S_2$ ), equation (i) reduces to:

$$m.C_v.\log_e \frac{T_2}{T_1} + mR \log_e \frac{V_2}{V_1} = 0$$

$$\text{Or, } m.C_v.\log_e \frac{T_2}{T_1} = -mR \log_e \frac{V_1}{V_2}$$

$$\text{Or, } C_v.\log_e \frac{T_2}{T_1} = R \log_e \frac{V_1}{V_2}$$

$$\text{Or, } \log_e \left( \frac{T_2}{T_1} \right)^{C_v} = \log_e \left( \frac{V_1}{V_2} \right)^R$$

$$\text{Or, } \left( \frac{T_2}{T_1} \right)^{C_v} = \left( \frac{V_1}{V_2} \right)^R$$

$$\text{Or, } \left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{R/C_v}$$

$$\text{Or, } \left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{(C_p - C_v)/C_v} = \left( \frac{V_1}{V_2} \right)^{(\gamma - 1)}$$

$$\text{Hence, } \left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{(\gamma - 1)} \dots\dots\dots (iii)$$

Similarly, for isentropic process, equation (ii) reduces to:

$$\left( \frac{T_2}{T_1} \right) = \left( \frac{P_1}{P_2} \right)^{[(\gamma - 1)/\gamma]} \dots\dots\dots (iv)$$

From (iii) and (iv)

$$PV^\gamma = \text{Constant}$$

## Change in Entropy for Liquid/Solid Water/Ice/Incompressible Substance

Using Conservation of Energy Equation,

$$\delta Q - \delta W = dU \dots\dots\dots (i)$$

From definition of entropy for reversible process,

$$dS = \frac{\delta Q}{T} \dots\dots\dots (ii)$$

From (i) and (ii),

$$T.dS = \delta W + dU$$

$$\text{Or, } T.dS = P.dV + dU \dots\dots\dots (iii)$$

For an incompressible substance,  $V_1=V_2$  Hence,  $dV=0$

Equation (iii) becomes

$$T.dS = dU$$

$$\text{Or, } T.dS = m.c.dT$$

$$\text{Or, } dS = m.c.\frac{dT}{T}$$

Integrating both sides,

$$\int_{S_1}^{S_2} dS = m.c.\int_{T_1}^{T_2} \frac{dT}{T}$$

$$\text{Or, } S_2 - S_1 = m.c.\log_e \frac{T_2}{T_1}$$

For constant temperature heat exchange, entropy change can be written as

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

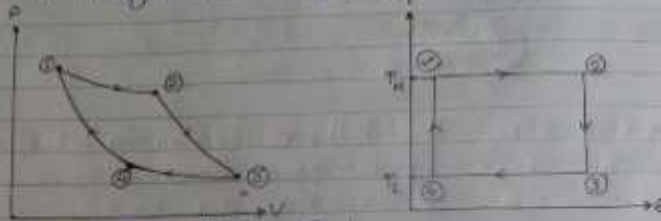
Integrating both sides,

$$S_2 - S_1 = \frac{Q(\text{net})}{T} = \frac{mL}{T}$$

## Carnot Cycle

- Process 1-2: Reversible isothermal expansion  
 Process 2-3: Reversible adiabatic expansion  
 Process 3-4: Reversible isothermal compression  
 Process 4-1: Reversible adiabatic compression

The P-V and T-s diagrams of Carnot Cycle are given below.



$$\begin{aligned}
 \text{Thermal efficiency } (\eta_{th}) &= \frac{W_{net}}{Q_{in}} = \frac{Q_{out}}{Q_{in}} \\
 \Rightarrow \eta_{th} &= \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \quad (i)
 \end{aligned}$$

To find  $Q_{in}$  and  $Q_{out}$ :

Process 1-2: Heat input  $Q_{in} = P_1 V_1 \log_e \frac{V_2}{V_1}$   
 Process 3-4: Heat output  $Q_{out} = P_3 V_3 \log_e \frac{V_3}{V_4}$

$\therefore$  From (i),  $\eta_{th} = 1 - \frac{T_3 \log_e \frac{V_3}{V_4}}{T_1 \log_e \frac{V_2}{V_1}} \quad (ii)$

To find  $\frac{V_3}{V_4}$  and  $\frac{V_2}{V_1}$ :

Process 1-2:  $T_1 = T_2 \quad (iii)$       Process 2-3:  $\frac{T_2}{T_3} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad (iv)$   
 Process 3-4:  $T_3 = T_4 \quad (v)$       Process 4-1:  $\frac{T_1}{T_4} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \quad (vi)$

$$\therefore \frac{V_3}{V_2} = \frac{V_4}{V_1} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

$$\therefore \eta = 1 - \frac{T_3}{T_1} = 1 - \frac{T_4}{T_2} = 1 - \frac{T_L}{T_H}$$

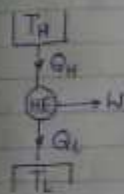


## Heat Engine and Thermal Efficiency

Heat engine is a device that operates in a cycle that produces work by transferring heat from a high to a low-temperature body.



Impossible.



Possible.

$$\eta_{th} = \frac{\text{output energy}}{\text{input energy}} = \frac{W}{Q_H} \quad (1)$$

Using Conservation of Energy,

$$Q_H = W + Q_L$$

$$\text{or } W = Q_H - Q_L$$

Using  $W$  in eqn (1) we get,

$$\eta_{th} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \rightarrow \text{actual thermal efficiency}$$

In the case of reversible heat engine (Carnot engine),

$$Q \propto T$$

$$\therefore Q_L \propto T_L \text{ and } Q_H \propto T_H$$

$$\eta_{th} = 1 - \frac{T_L}{T_H} \rightarrow \text{maximum possible efficiency of heat engine}$$

$\eta_a < \eta_{max}$  : Irreversible Heat Engines

$\eta_a = \eta_{max}$  : Reversible Heat Engines

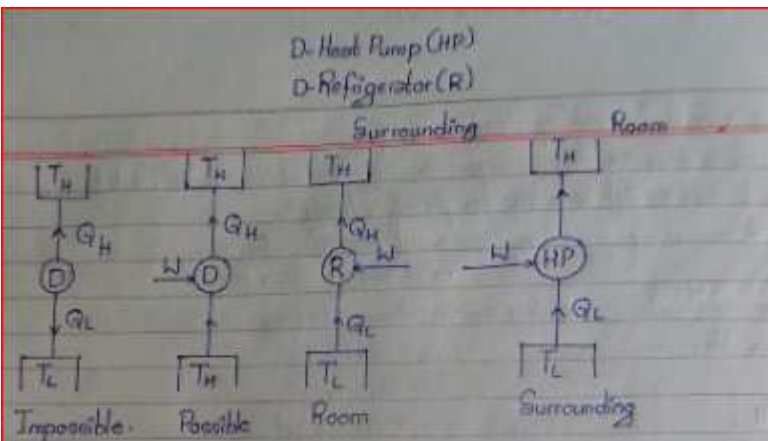
$\eta_a > \eta_{max}$  : Impossible Heat Engine

## Heat Pump

It is a reversed heat engine that requires work and accomplishes the objective of transferring heat from a low to a high-temperature body with a purpose to provide heat transfer to the higher temperature region.

## Refrigerator

It is a device that operates in a cycle that requires work and accomplishes the object of transferring heat from a low to a high-temperature body with a purpose to cause heat transfer from the lower temperature region.



Coefficient of Performance (COP) of Heat Pump

$$\text{COP} = \frac{\text{Desired Effect}}{\text{Required Input}} = \frac{Q_H}{W} \quad (1)$$

Using Conservation of Energy

$$W + Q_L = Q_H$$

$$\text{or, } W = Q_H - Q_L$$

Using  $W$  in eqn. (1), we get,  $(\text{COP})_{\text{HP}} = \frac{Q_H}{Q_H - Q_L}$

For reversible heat pump,  $Q \propto T$

$$\therefore (\text{COP})_{\text{HP}} = \frac{T_H}{T_H - T_L} \Rightarrow \text{maximum possible COP.}$$

Similarly,

$$(\text{COP})_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$(\text{COP})_R = \frac{T_L}{T_H - T_L} \Rightarrow \text{max. possible COP of refrigerator}$$

$$\therefore (\text{COP})_{\text{HP}} = (\text{COP})_R + 1.$$

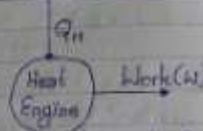
### Kelvin-Planck Statement

"It is impossible to construct a heat engine that is operated in a cycle and converts all heat input into work without expenditure to the surroundings."

- a. Work can be done by the transfer of heat only if there are two temp levels, and heat is transferred from the high temp body to the heat engine, to the low temperature body from the heat engine.

- b. It is impossible to build a heat engine that has a thermal efficiency of 100%.

High Temperature Reservoir  
(source at  $T_H$ )



Impossible to construct such device. Such device is known as P.M.M.2.

Note that the impossibility of having a 100% efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.

### Clausius Statement

"It is impossible to construct a device that is operated in a cycle and transfers heat from lower temperature reservoir to higher temperature reservoir without expenditure of external energy."

- It implies that COP of the refrigerator or heat pump is always less than infinity.

- Heat itself cannot flow from a lower to a higher temperature.

High Temp. Reservoir  
(source at  $T_H$ )



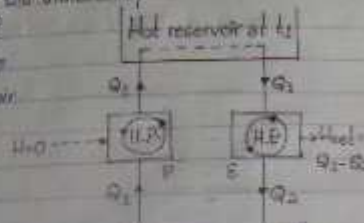
Low Temp. Reservoir  
(sink at  $T_L$ )

Impossible

### Equivalence of the Clausius Statement and Kelvin-Planck Statement

Kelvin-Planck and the Clausius statements are equivalent in their consequences. The equivalence can be proved by the theory that the truth of each statement implies the truth of the other, or if the violation of one statement implies the violation of the other.

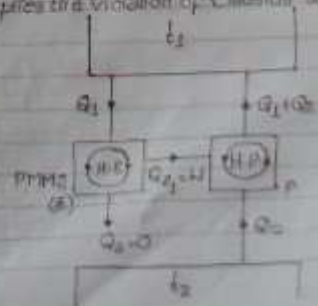
1. The violation of Clausius statement implies the violation of Kelvin-Planck Statement.  
Let us first consider a cyclic heat pump  $P$  which transfers heat from a low temperature reservoir ( $t_2$ ) to a high temperature reservoir ( $t_1$ ) with no other effect, i.e. with no expenditure of work, violating Clausius statement.



Let us assume a cyclic heat engine  $E$  operating between the same thermal energy reservoirs, producing  $W_{net}$  in one cycle. The rate of working of the heat engine is such that it draws an amount of heat  $Q_1$  from the hot reservoir equal to that discharged by the heat pump. Then the hot reservoir may be eliminated and the heat  $Q_1$  discharged by the heat pump is fed to the heat engine. So we see that the heat pump  $P$  and the heat engine  $E$  acting together constitute a heat engine operating in cycles and producing net work while exchanging heat only with one body at a single fixed temperature. This violates the Kelvin-Planck Statement.

2. The violation of Kelvin-Planck statement implies the violation of Clausius statement.

Let us now consider a perpetual motion machine of the second kind ( $E$ ) which produces net work in a cycle by exchanging heat with only one thermal reservoir (at  $t_1$ ) and thus violates the Kelvin-Planck statement.



Let us assume a cyclic heat pump ( $P$ ) extracting heat  $Q_2$  from a low temperature reservoir at  $t_2$  and discharging heat to the high temperature reservoir at  $t_1$  with the expenditure of work  $W$  equal to what the PMM2 delivers in a complete cycle. So  $E$  and  $P$  together constitute a heat pump working in cycle and producing the sole effect of transferring heat from a lower to a higher temperature body, thus violating the Clausius statement.