

Thermodynamics - II

From 1st law, we have learnt that when heat is converted to work,

Work done \equiv Heat absorbed.

$$W = JH$$

where $W =$ work, $H =$ heat

$J =$ mechanical equivalent of heat

From experiments, it has been observed that the heat absorbed cannot be

completely converted into work w.o.
leaving some changes in the system or
surroundings.

Various statements of the Second Law
of Thermodynamics -

1. All spontaneous process takes the flow
of heat from hot end to cold
end, diffusion of gas from high
pressure to low pressure,

flow of water downhill etc. are thermodynamically irreversible -

Spontaneous process is a process that occurs w.o. the help of any external energy.

2. The complete conversion of heat into work is impossible w.o. leaving some effects on the system

3. It is impossible to construct a machine functioning in cycles, which can convert heat completely into equivalent amount of work producing changes elsewhere.

4. Without the use of any external agency, heat cannot by itself pass from a colder to hotter body.

Efficiency of an engine

The fraction of heat absorbed by a machine that it can transform into work is called the efficiency of a machine.

Say $Q =$ heat absorbed by a system
 $W =$ work done.

$$\text{Efficiency } (\eta) = \frac{W}{Q}$$

Heat engine: A machine that is used to convert heat to work is called heat engine -

In order to bring about the conversion of heat to work, the machine has to absorb heat from a heat reservoir at a higher temperature called the source -

Source & Sink

Energy absorbed

Work

Heat Engine

Residual heat

Heat reservoir

T_1

Heat reservoir at lower temp.

T_2

Source

T_1

T_2

source > sink.

Sink

The temperature of the source > sink.

Sink: A hypothetical body of infinitely large mass capable of absorbing or rejecting unlimited quantities of heat without undergoing appreciable changes.

Source \equiv Reservoir that supplies

Sink \equiv " that absorbs energy

The Carnot Cycle

Step I → Step II

$T = \text{constant}$

Volume expands

Isothermal

expansion.

Step II → Step III

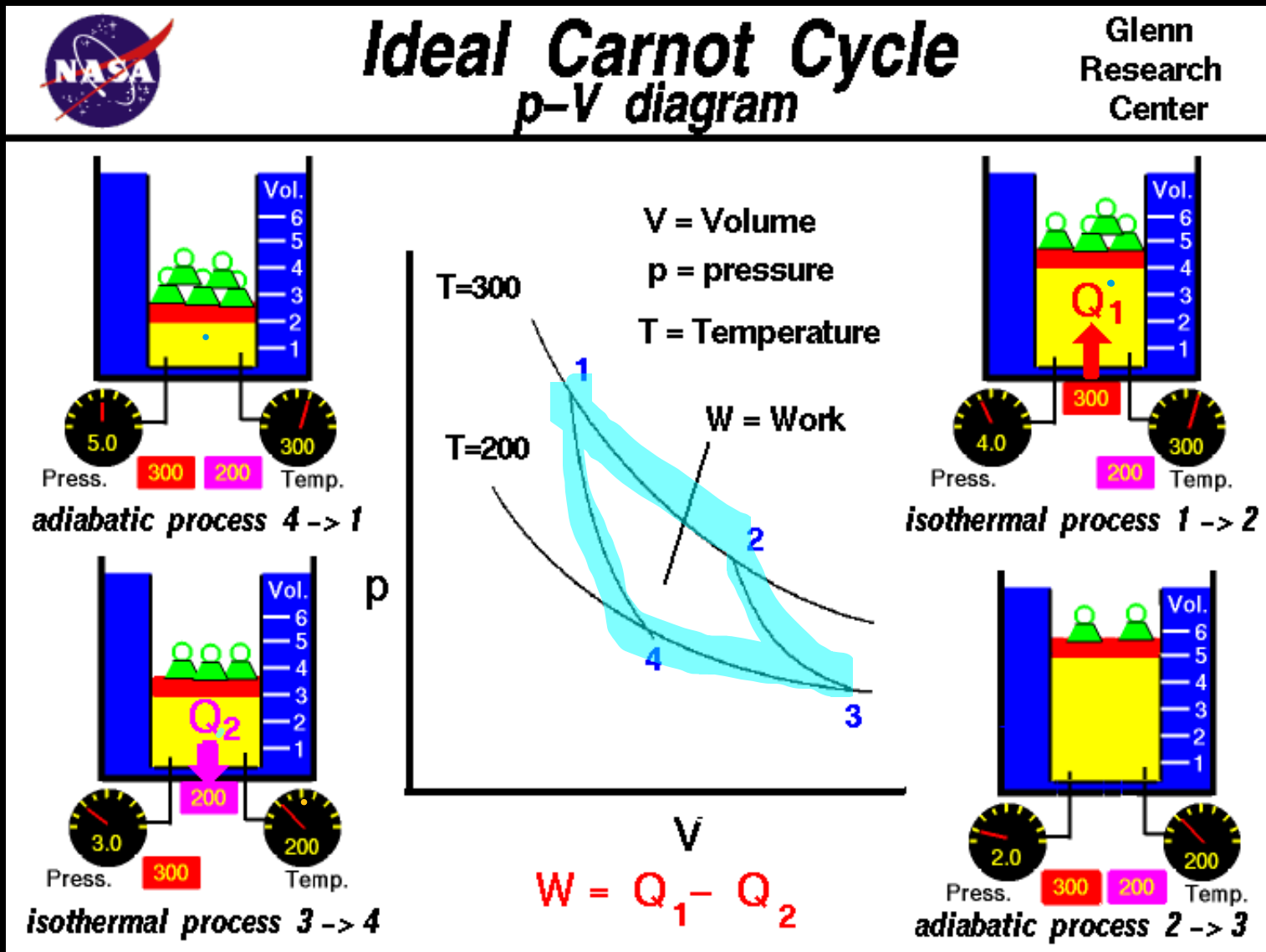
Adiabatic expansion

Step III → Step IV

Isothermal Compression

Step IV → Step I

Adiabatic



A Carnot cycle is a process in which the system returns to its original state after a number of successive changes. A process conducted in this manner is called a cycle process -

A Carnot Engine consists of a cylinder containing 1 mol of an ideal gas as the working substance.

It consists of a frictionless piston.

so that all operations can be carried out in reversible manner.

Carnot engine - is also called as reversible heat engine

The cylinder is insulated on all sides except for the bottom so that heat can flow to or from the system only through the bottom.

Carnot engine: Heat Reservoir

There are
2 heat
reservoir

Higher temp.

Lower Temp.

T_2

$T_2 > T_1$

T_1

Source

Sink.

adiabatic

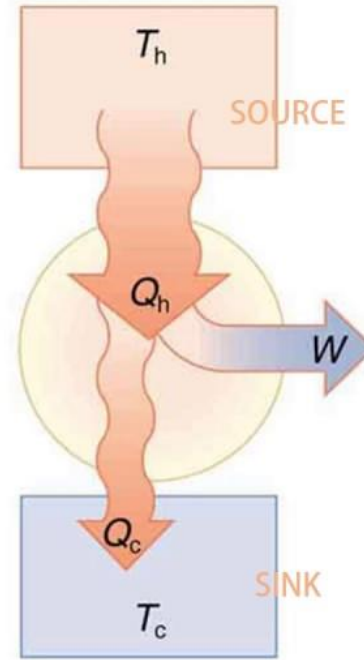
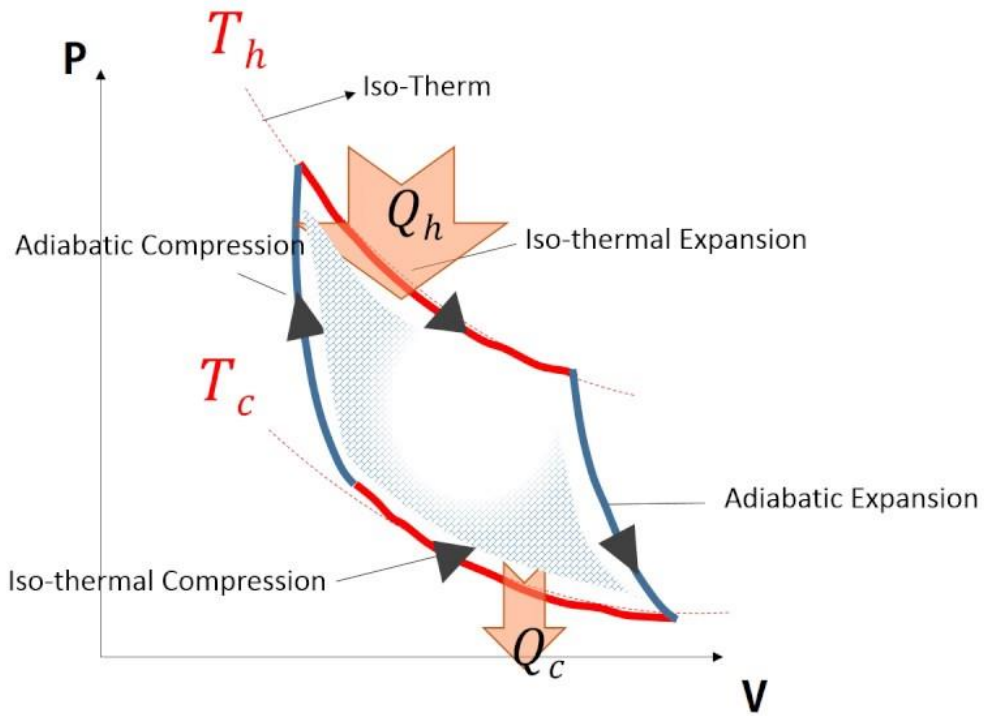
Operation

Isothermal

Placing the cylinder in source or sink so that heat exchange occurs & temp. remains constant

The cylinder is placed on insulating material so that no heat transfer occurs

Carnot Cycle and Heat Engine



$$\eta \text{ (efficiency)} = 1 - \frac{T_c}{T_h}$$

Carnot cycle
has four
different
steps.

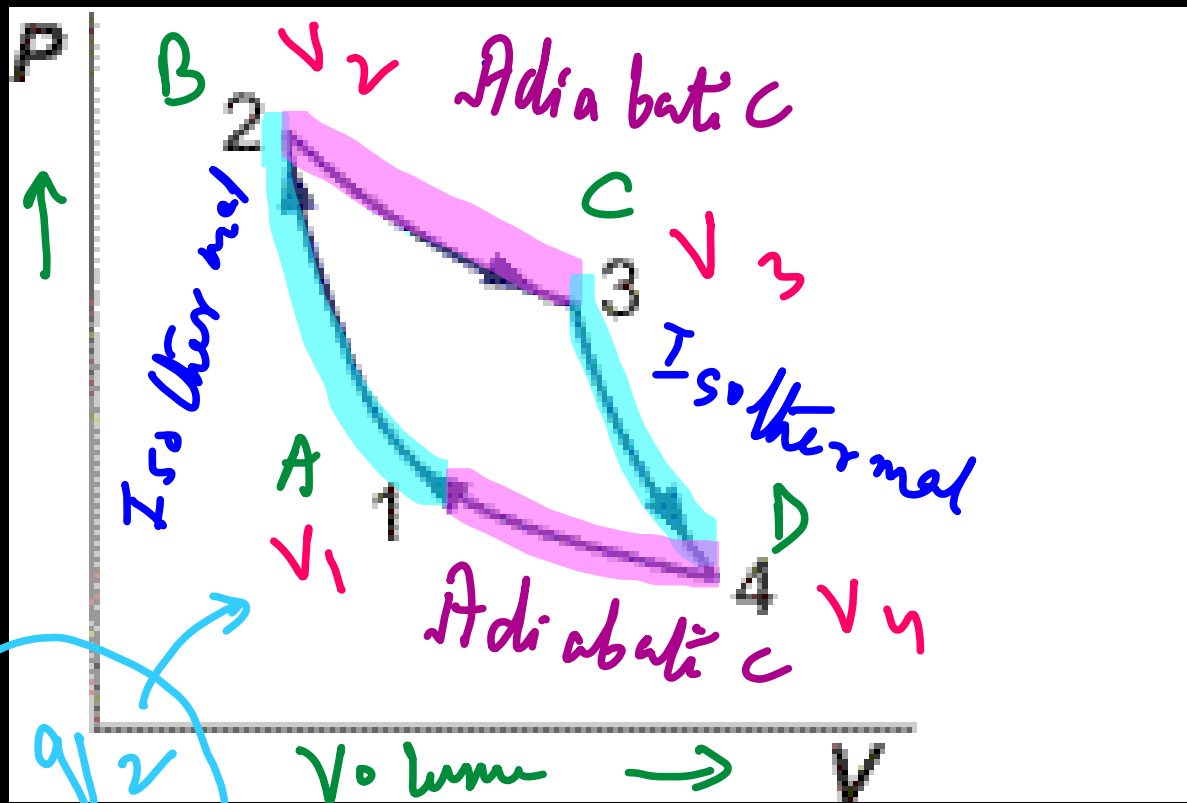
1. Isothermal
Expansion

2. Adiabatic
Compression

expansion

3. Isothermal

4. Adiabatic
compression.



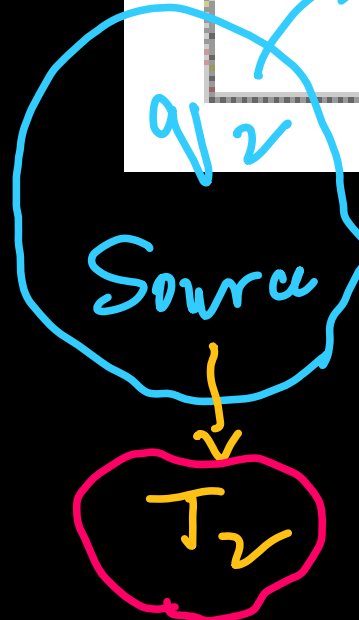
Step I: Isothermal
Expansion ($v_1 \rightarrow v_2$)

$$w_1 = RT \ln \frac{v_2}{v_1}$$

For an ideal gas,

$$\text{Work done} = \text{Heat absorbed}$$

$$w = q_2 = RT \ln \frac{v_2}{v_1}$$



The gas absorbs heat q_2 from source & expands isothermally & reversibly until its volume reaches v_2

Step - II: Adiabatic expansion $V_2 \rightarrow V_3$

The cylinder is now removed from source and placed in perfectly insulating material so that the gas expands adiabatically & reversibly. Work is done in the expansion but since no heat enters or leaves the system, the temp. must fall. The reversible

adiabatic expansion is continued till the temperature has fallen to T_2 , which is the temperature of the sink.

Work done,

$$W_2 = C_v(T_2 - T_1)$$

where C_v = heat capacity of the ideal gas.

III. Isothermal Compression $V_3 \rightarrow V_4$
The cylinder is now removed from the

insulating material & placed in contact with the sink. The gas is compressed isothermally & reversibly until the volume changes from V_3 \rightarrow V_4 .

heat returned to sink



$$-Q_3 = RT_1 \ln \frac{V_4}{V_3}$$

$$= -Q_3 = RT_1 \ln \frac{V_4}{V_3}$$

Step IV: Adiabatic compression -

The cylinder is again removed from the sink and placed on the insulating material.

The gas is compressed adiabatically from $v_4 \rightarrow v_1$.

$$Q_4 = C_v (T_1 - T_2) \\ = - C_v (T_2 - T_1)$$

$Q = 0$
↓
adiabatic

Net work done,

$$w = w_1 + w_2 + w_3 + w_4$$

$$= R T_2 \ln \cdot \frac{V_2}{V_1} + C_{v2} (T_2 - T_1) \\ + R T_1 \ln \cdot \frac{V_4}{V_3} - C_{v1} (T_2 - T_1)$$

$$= R T_2 \ln \cdot \frac{V_2}{V_1} + R T_1 \ln \cdot \frac{V_3}{V_3}$$

\therefore v_1 & v_4 lies on the
 adiabatic curve & v_3 & v_2
 lies on another, we can write

$$\left(\frac{v_3}{v_1} \right)^{\gamma-1} = \frac{T_2}{T_1} \quad \text{(i)} \quad \left(\text{adiabatic } v-T \text{ relationship} \right)$$

$$\& \left(\frac{v_3}{v_2} \right)^{\gamma-1} = \frac{T_2}{T_1} \quad \text{(ii)}$$

Comparing (i) & (ii), we have

$$\left(\frac{V_4}{V_1} \right)^{\delta-1} = \left(\frac{V_3}{V_2} \right)^{\delta-1}$$

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

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

$$\begin{aligned} \omega &= R T_2 \ln \frac{V_2}{V_1} + R T_1 \ln \frac{V_3}{V_2} \\ &= R T_2 \ln \frac{V_2}{V_1} + R T_1 \ln \frac{V_1}{V_2} \end{aligned}$$

$$= R T_2 \ln \frac{V_2}{V_1} - R T_1 \ln \frac{V_2}{V_1}$$

$$\omega = R \ln \frac{V_2}{V_1} (T_2 - T_1) \rightarrow \text{(iii)}$$

$$\omega_1 = \gamma_2 \varepsilon = R T_2 \ln \frac{V_2}{V_1} \rightarrow \text{(iv)}$$

$$\frac{W}{Q_2}$$

$$= \frac{\cancel{R} \ln \frac{V_2}{V_1} (T_2 - T_1)}{\cancel{R} T_2 \ln \frac{V_2}{V_1}}$$

$$= \frac{T_2 - T_1}{T_2} \rightarrow \text{efficiency}$$

Efficiency of heat engine.

engine depends only on the

The efficiency of heat engine depends only on the

temperature T_1 of source & sink.

The efficiency of a heat engine is always less than unity.

$$\Rightarrow \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$$
$$= 1 - \frac{T_1}{T_2}$$
$$\because T_2 > T_1$$
$$\frac{T_1}{T_2} < 1 \quad \therefore 1 - \frac{T_1}{T_2} < 1$$

Car not's Theorem

The efficiency of a reversible heat engine depends only on the temperature of the source and the sink and is independent of the nature of the working substance

$$\eta = \frac{T_2 - T_1}{T_2}$$

All reversible heat engines working between the same two temperatures will have the same efficiency.

Q/ Calculate the maximum efficiency of a steam engine operating between 110° and 25°C . What would be the efficiency of the engine if the boiler temperature is raised to 140°C , the temperature

of the sink remaining the same.

Solⁿ

Working formula:

$$\eta = \frac{T_2 - T_1}{T_1}$$

Case I

$$T_1 = 25^\circ\text{C} = 25 + 273 = 298 \text{ K}$$

$$T_2 = 110^\circ\text{C} \quad 273 + 110 = 383 \text{ K}$$

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{383 - 298}{383} = 0.222 = 22.2\%$$

Case II

$$T_1 = 25^\circ \text{C} = 298 \text{ K}$$

$$T_2 = 140^\circ \text{C} = 413 \text{ K}$$

$$\eta = \frac{413 - 298}{298} = 0.278$$

$$= 27.8 \%$$

Q. Calculate the amount of heat supplied to Carnot's cycle working between 300 K & 200 K if the maximum

work obtained is 895 J

SNⁿ

work

Working formula:

$$\eta = \frac{w}{q_2}$$

Temp. of source

Temp of sink

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$= \frac{T_2 - T_1}{T_2}$$

heat

known

$$\frac{895}{q_2} = \frac{368 - 288}{368}$$

$$T_1 = 288 \text{ K}$$

$$T_2 = 368 \text{ K}$$

$$\Rightarrow q_2 = \frac{895}{0.217} = 4124 \text{ J}$$

How Carnot Cycle leads to the definition of Entropy:

For a reversible Carnot cycle working between temperatures T_1 & T_2 ,

$$\frac{q_2 - q_1}{q_1} = \frac{T_2 - T_1}{T_2}$$

where q_2 is othermally q_2 at temp. T_2 and q_1 is

the heat absorbed isothermally, at $\bar{v}_1 \cdot T_1$,
and reversibly

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\Rightarrow \cancel{q_1} / \cancel{q_2} = \cancel{T_2} / \frac{T_1}{T_2}$$

$$\Rightarrow \frac{q_1}{q_2} = \frac{T_1}{T_2}$$

$$\Rightarrow \frac{q_1}{T_1} = \frac{q_2}{T_2} \Rightarrow \frac{q}{T} = \text{constant}$$

The heat absorbed or lost is otherwise
 and reversibly by the temp. at which
 the heat is absorbed or lost is a
 constant quantity for a particular
 system.

Heat absorbed
 at temp. T_2

$$\frac{q_2}{T_2}$$

=

$$\frac{q_1}{T_1}$$

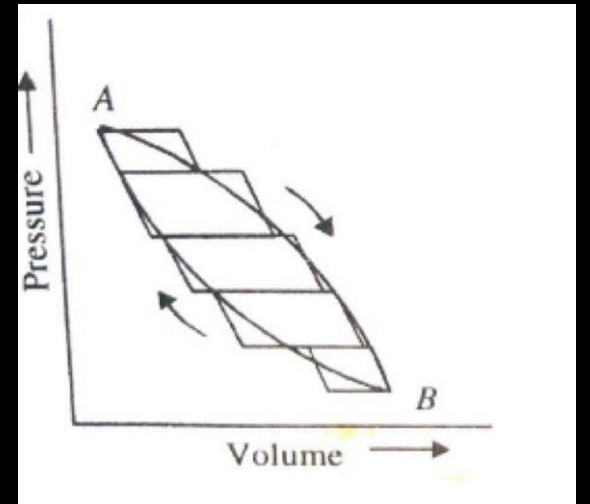
heat lost at
 temp. T_1

If $\frac{q_1}{T_1}$ were heat absorbed at temp. -
 we can rewrite the above eqn -

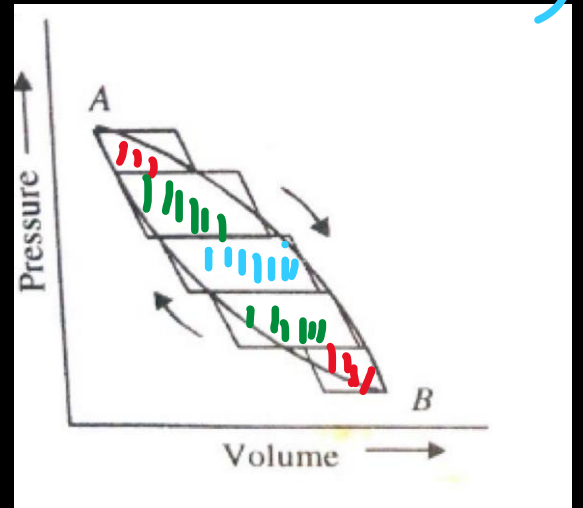
$$\frac{q_2}{T_2} = - \frac{q_1}{T_1}$$

$$\Rightarrow \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0 \Rightarrow \sum \frac{q}{T} = 0$$

Let us consider any reversible cycle ABA. It may be considered to be made up of a number of Carnot cycles. Starting from A



and going through all the cycles successively from $A \rightarrow B$, it can be shown that all paths inside the closed curve $AB A$ cancel each other leaving only the zigzag outer path. The zigzag path is almost the same as path $AB A$ of the reversible cycle.



If we increase the no. of Carnot cycles & make them smaller, it can be made to match more closely to ABA.

The reversible cycle can be regarded as being made up by infinite no. of Carnot cycles. For each of these cycles,

For infinite no. of Carnot cycles,

$$\sum \frac{q}{T} = 0$$

$$\sum \frac{\delta q}{T} = 0 \quad \text{where } \delta q \text{ is a very small quantity } \rightarrow$$

Further the above term may be divided into two parts \rightarrow

1) for path $A \rightarrow B$

2) " " $B \rightarrow A$

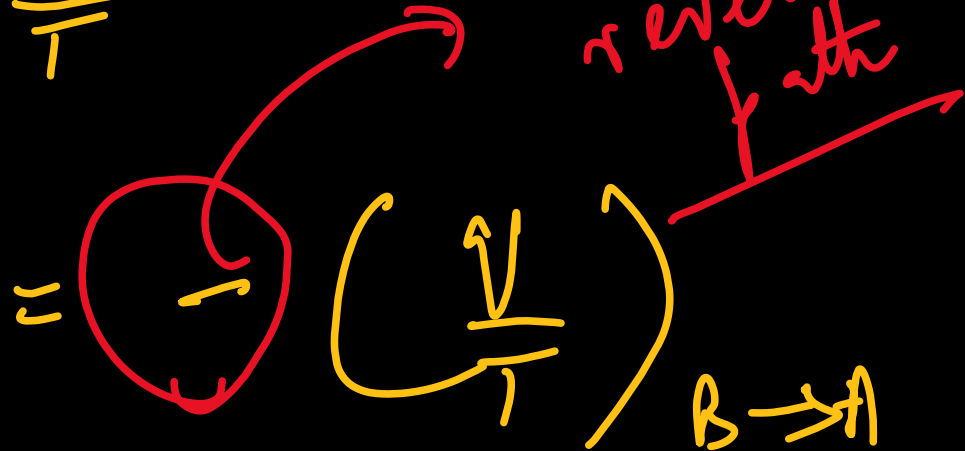
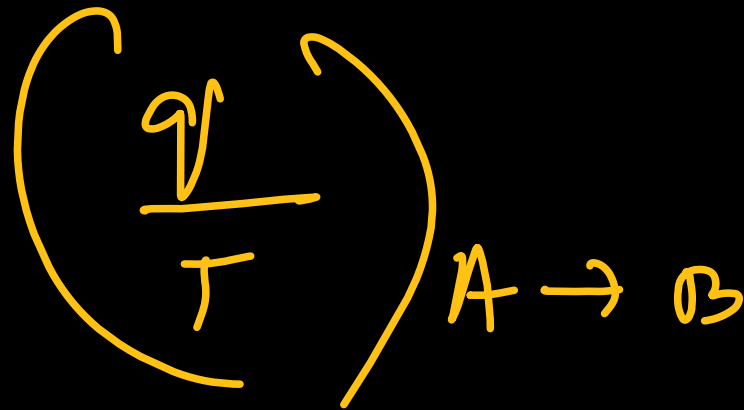
$$\sum \frac{\delta q}{T} = \sum_{A \rightarrow B} \frac{\delta q}{T} + \sum_{B \rightarrow A} \frac{\delta q}{T} = 0$$

\Rightarrow

$$\sum_{A \rightarrow B} \frac{\delta q}{T} = - \sum_{B \rightarrow A} \frac{\delta q}{T}$$



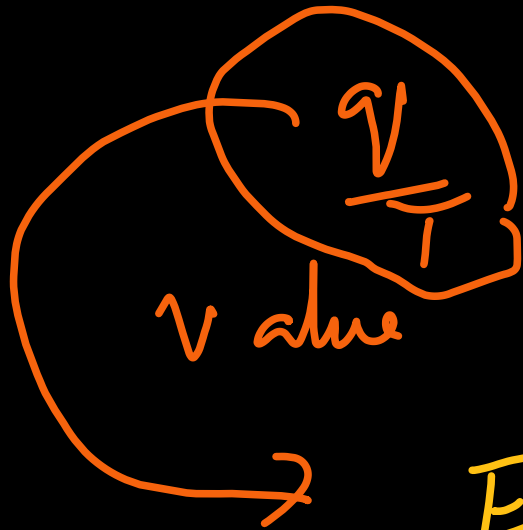
\Rightarrow



\Rightarrow

The total value of the quantity $\frac{q}{T}$ for path $A \rightarrow B$ is equal to the quantity $\frac{q}{T}$ for the reverse path $B \rightarrow A$.

The quantity q/T is a state function
 i.e. its value depends only
 on the initial state A & final state
 B. & is independent of path.
 change depends on the



of P, V, T. $S_A =$ value of entropy at A
 $S_B \rightarrow$ entropy at B
Entropy
 $\frac{q}{T} = S_B - S_A = \Delta S$

Entropy is a state function.

Entropy change can be defined as the quantity of heat absorbed isothermally and reversibly divided by the absolute temperature at which heat is absorbed.

$\Delta S =$
state function

$$\frac{q}{T}$$

Based on Carnot cycle the heat absorbed is reversible.

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Rightarrow ds = \frac{q_{rev}}{T}$$

Entropy change is rated only when heat is absorbed reversibly.

Entropy is the tendency of a system to move from ordered to disordered state i.e. the degree of randomness.

Net entropy change for a reversible process

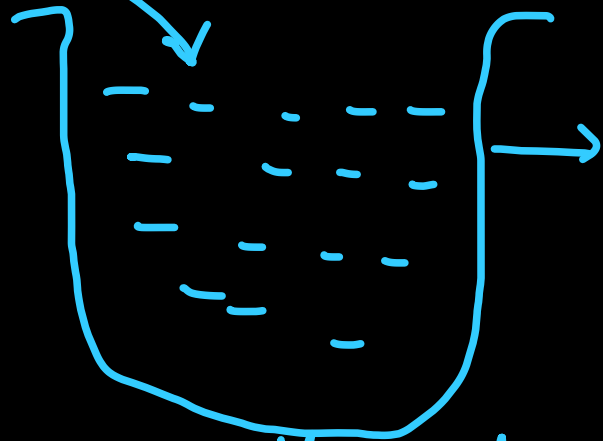
Q Prove that for a reversible process, net entropy change for the system and surrounding is zero.

Solⁿ
= Heat absorbed by a system
" lost by the surrounding.

Once practical
an analogy -



10°C



80°C

If you drop a ball at 10°C to
a beaker containing water at 80°C -

Observation ?

Heat gained by the ball =
" lost by water ,

Principle
of
calorimetry.

$$\Delta S_{\text{surrounding}} = - \frac{q_{\text{rev}}}{T}$$

∴ Net entropy change

$$= \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}}$$

$$= \frac{q_{\text{rev}}}{T} + \left(- \frac{q_{\text{rev}}}{T} \right) = 0$$

∴ In a reversible process, the net entropy is zero.

Entropy change for irreversible process

Let us suppose that the total heat lost by the surrounding is q_{irrev} . This heat is absorbed by the system but entropy change of the system does not depend on the heat actually absorbed but it depends upon the heat absorbed reversibly i.e. q_{rev} .

Thus, if the heat is absorbed isothermally by the system, the absolute temp T , the entropy change of the system will be -

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

Let us suppose that the loss of heat q_{irrev} place in finite time by the surrounding takes slowly because

the surroundings are much bigger in size and magnitude compared to the system and isothermally at temp. T .

∴ Entropy change of the surrounding is given by -

$$\Delta S_{\text{surrounding}} = - \frac{q_{\text{irrev}}}{T}$$

∴ Net entropy change of the combined system and surrounding

will be

$$\Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} \\ = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irrev}}}{T}$$

From 1st law, we know that work done in a reversible process is maximum work.

$$W_{\text{rev}} > W_{\text{irrev}}$$

As internal energy is a state function, the value of ΔU remains same whether the process is carried out reversibly or irreversibly.

$$\Delta U = q_{\text{rev}} - w_{\text{rev}}$$

$$= q_{\text{irrev}} - w_{\text{irrev}}$$

$$\therefore q_{\text{rev}} - w_{\text{rev}} = q_{\text{irrev}} - w_{\text{irrev}}$$

$$\therefore \omega_{rev} > \omega_{irrev}$$

$$\therefore q_{rev} > q_{irrev}$$

$$\Rightarrow \frac{q_{rev}}{T} > \frac{q_{irrev}}{T} \quad \left(\text{dividing both sides by } T \right)$$

$$\Rightarrow \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} > 0$$

$$\Rightarrow \Delta S_{sys} + \Delta S_{surr} > 0$$

In an irreversible process, the entropy change for the combined system & surroundings is greater than zero.

$$\Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$

An irreversible process is accompanied by a net increase of entropy.

Reversible process = Slow



Irreversible process \rightarrow fast conversion.
of substrate to product.

This process is more spontaneous -
All spontaneous processes are accompanied
by a net increase in entropy.

Q. Entropy of the universe is constantly increasing - Explain.

All process that occur in nature are thermodynamically irreversible and are accompanied with increase in entropy. The entropy of the universe is constantly increasing.

Summing up first law & second law in
context of universe -

The energy of the universe is
constant where as the entropy of
the universe is constantly increasing
and tends to maximum value.

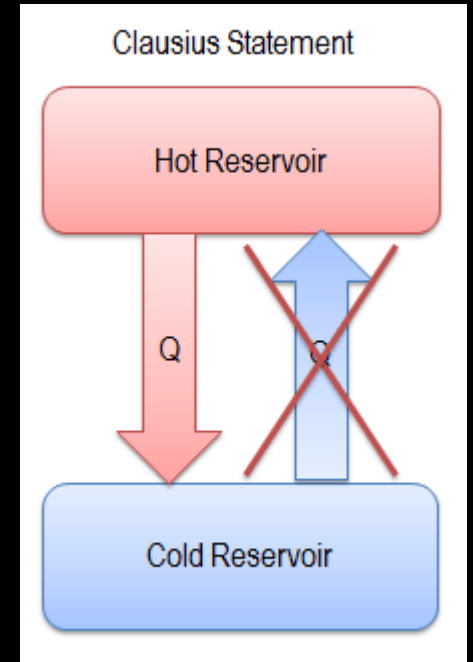
Thermodynamics Second Law:

Clausius Statement:

It is impossible for heat to move by itself from a lower temperature reservoir to a higher temperature reservoir. i.e. heat transfer can only occur spontaneously in the direction,

of temperature decrease,
For e.g., we cannot
construct a refrigerator
that operates without
any work input.

Clausius statement tells us about
the direction of heat flow.



Kelvin Planck Statement

It is impossible for a system to receive a given amount of heat from a high temperature reservoir and to provide an equal amount of work output. While a system converting work to an equivalent energy transfer as

heat is possible, a device converting heat to an equivalent energy transfer as work is impossible.

The thermal efficiency of a heat engine cannot be 100%.

Entropy change for an ideal gas under different conditions:

Let us consider 1 mole of an ideal gas enclosed in a cylinder fitted with a frictionless piston. If a small amount of heat δq_{rev} is supplied to the system reversibly &

isothermally, at the temperature T ,
then entropy change accompanying
the process is -

$$ds = \frac{\delta q_{rev}}{T}$$

According to first law of thermodynamics,
→ internal energy

$$= du + \delta w \rightarrow \text{work}$$

heat absorbed

$$\delta q_{rev}$$

considering the process is carried
out reversibly

$$ds = \frac{\delta q_{rev}}{T} = \frac{du + \delta w}{T}$$

$$\therefore \delta w = P dv \quad \left(\begin{array}{l} \text{if the work is} \\ \text{related to work} \\ \text{of expansion} \end{array} \right)$$

$$\Rightarrow ds = \frac{du + P dv}{T}$$

$$\Rightarrow \underbrace{T ds}_{\delta q_{rev}} = \underbrace{du}_{\delta u} + \underbrace{P dv}_{\delta w} \quad \rightarrow \textcircled{1}$$

of an ideal gas

$$C_v = \frac{du}{dT} \Rightarrow du = C_v dT$$

where C_v = molar heat capacity
at constant volume -

For an ideal gas, $Pv = RT$

$$\Rightarrow P = \frac{RT}{v}$$

where v is the volume of the system at temperature T & pressure P ; R = universal gas constant

$$ds = \frac{\delta q_{rev}}{T} = \frac{du + PdV}{T}$$

$$\Rightarrow ds = \frac{C_v dT}{T} + \frac{P}{T} dV$$

$$= C_v \frac{dT}{T} + \frac{RT}{V} dV$$

$$\Rightarrow ds = C_v \frac{dT}{T} + R \frac{dV}{V}$$

If the volume changes from $V_1 \rightarrow V_2$
when temperature " " $T_1 \rightarrow T_2$

We can write

$$\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} C_v \frac{dT}{T} + \int_{v_1}^{v_2} R \frac{dv}{v}$$
$$= C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

$$\Rightarrow \Delta S = C_v \cdot \ln \cdot \frac{T_2}{T_1} + R \ln \cdot \frac{v_2}{v_1}$$

where $\Delta S = s_2 - s_1$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2}$$

$$\Rightarrow \frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$= (C_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2}$$

$$\Rightarrow \Delta S = (c_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2}$$

$$\begin{aligned} \Rightarrow \Delta S &= c_p \ln \frac{T_2}{T_1} - \cancel{R \ln \frac{T_2}{T_1}} \\ &\quad + \cancel{R \ln \frac{T_2}{T_1}} + R \ln \frac{P_1}{P_2} \\ &= c_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \end{aligned}$$

$$\Delta S = C_{v0} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$
$$= C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

Isothermal change: $\Delta T = 0 \therefore T_1 = T_2$

$$\therefore \Delta S = R \ln \frac{V_2}{V_1}$$

Isochoric change: $\Delta V = 0 \therefore V_1 = V_2$

$$\Delta S = C_{v0} \cdot \ln \frac{T_2}{T_1}$$

Für isobare Prozess, $P_1 = P_2 \therefore \Delta P = 0$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

Process

1. Isothermal
2. Isobaric
3. Isochoric

Entropy change

$$\Delta S = R \ln \frac{v_2}{v_1}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

Entropy change during change of phase

Solid \rightleftharpoons Liquid

Liquid \rightleftharpoons Gas

Solid \rightarrow Gas



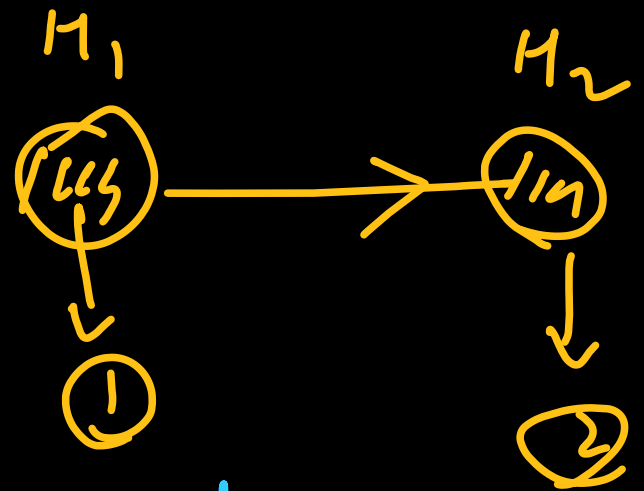
Connecting Enthalpy & Entropy

$$ds = \frac{dq_{rev}}{T} = \frac{du + PdV}{T}$$

$$= U + PV$$

$$H_1 = U_1 + PV_1$$

$$H_2 = U_2 + PV_2$$



enthalpy (H) of the system

Enthalpy change of a system is equal to the heat added at constant pressure.

absorbed at constant pressure.

$$\Delta H = H_2 - H_1$$

$$\Delta H = q_p$$

$$= (U_2 + P V_2) - (U_1 + P V_1)$$

$$= (U_2 - U_1) + P (V_2 - V_1)$$

$$= \Delta U + P \Delta V$$

$$dH = du + P dv$$

$$ds = \frac{dq_{rev}}{T} = \frac{du + p dv}{T}$$

$$= \frac{dH}{T}$$

$$\Rightarrow \Delta S = \frac{\Delta H}{T}$$

For melting, $\Delta S_m =$

latent heat of
melting

$$\frac{\Delta H_m}{T_m}$$

melting temperature

Vaporisation:

$$\Delta S_v = \frac{\Delta H_v}{T_v}$$

Entropy of vaporisation

Latent heat of vaporisation

Process like melting or evaporation involve absorption of heat, which is taken as +ve sign convention.

Therefore ΔS for these processes are +ve
For the reversible process, such as
freezing or condensation, evolution of
heat will occur. So these processes
are considered as negative and accompanied
by decrease in entropy.

-
- ✓ 1. Internal energy = U
 - ✓ 2. Enthalpy = H

Entropy: S

Work Function / Helmholtz Free energy

$$A = U - TS$$

Where $U =$ internal energy

$S =$ entropy

Let us consider an isothermal
change taking place at temperature
 T .

$$A_1 = U_1 - TS_1 \quad (\text{initial state})$$

$$A_2 = U_2 - TS_2 \quad (\text{final state})$$

where A_1 , U_1 & S_1 are respectively
 the work function, internal energy,
 & entropy of the system in the
 initial state & A_2 , U_2 & S_2
 are the corresponding values for
 final state.

$$A_1 = U_1 - TS_1$$

$$A_2 = U_2 - TS_2$$

$$\begin{aligned}
 & A_2 - A_1 \\
 &= (U_2 - TS_2) \\
 &\quad - (U_1 - TS_1)
 \end{aligned}$$

$$\begin{aligned} A_2 - A_1 &= (U_2 - TS_2) - (U_1 - TS_1) \\ &= U_2 - TS_2 - U_1 + TS_1 \\ &= (U_2 - U_1) - T(S_2 - S_1) \end{aligned}$$

$$\Rightarrow A_2 - A_1 = \Delta U - T\Delta S$$

$$\therefore \Delta S = \frac{q_{rev}}{T} = \frac{\Delta U + w_{max}}{T}$$

$$q_{rev} = \Delta U + \omega_{max}$$

$$\Rightarrow \Delta U = q_{rev} - \omega_{max}$$

$$\Delta A = \Delta U - T \Delta S$$

$$= \cancel{q_{rev}} - \omega_{max}$$

$$\Delta A = -\omega_{max}$$

$$\Rightarrow -\Delta A = \omega_{max}$$

Reversible
work is
maximum
work

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Rightarrow T \Delta S = q_{rev}$$

For a process occurring at constant temperature, the decrease in work function A is equal to the maximum work done by the system.

Gibb's Free Energy

Gibb's free energy, ' G '

$$G = H - TS$$

↑ enthalpy
→ entropy

↓ temp.

Since H , T , & S are functions of the state only $\therefore G$ is also a state function.

For an isothermal process occurring at temperature T ,

$$G_1 = H_1 - TS_1 \rightarrow \text{initial state}$$

$$G_2 = H_2 - TS_2 \rightarrow \text{final "}$$

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$

$$= (H_2 - H_1) - T(S_2 - S_1)$$

$$\Rightarrow \boxed{\Delta G = \Delta H - T \Delta S}$$

Physical significance of Gibbs free energy: At constant temp! T .

$$\Delta G = \Delta H - T \Delta S$$

$$= \Delta U + P \Delta V - q_{rev}$$

$$= \left(\Delta U - q_{rev} \right) + P \Delta V$$

From 1st law, $q = \Delta U + w$

$$q_{rev} = \Delta U + w_{max}$$

$$\Rightarrow \Delta U - q_{rev} = -w_{max}$$

$$\therefore \Delta G = -w_{max} + P \Delta V$$

$$-\Delta G = w_{\max} - P\Delta V \rightarrow \text{work of expansion}$$

$P\Delta V$ is the work of expansion done by the system corresponding to the increase in volume ΔV .

Hence $w_{\max} - P\Delta V$ stands for the maximum work other than the work of expansion. This is called the maximum

useful work available from the process.
 For a process occurring at constant
 temperature and constant pressure
 the decrease in Gibbs free energy
 is equal to the maximum useful
 work obtainable from the process

$$\therefore -\Delta G = W_{\text{max}} - P\Delta V$$

Max useful work = Total work - work of expansion

$$A = U - TS \quad \rightarrow \quad \text{max work}$$

$$G = H - TS \quad \rightarrow \quad \text{max useful}$$

$$\therefore \Delta A = \Delta U - T\Delta S \rightarrow \text{work}$$

$$\Delta G = \Delta H - T\Delta S \rightarrow \text{②}$$

$$\therefore \Delta G - \Delta A = \Delta H - \cancel{T\Delta S}$$

$$\Delta G - \Delta A$$

$$P\Delta V$$

$$= \Delta H - \Delta U = \cancel{\Delta U} + P\Delta V = \Delta U$$