

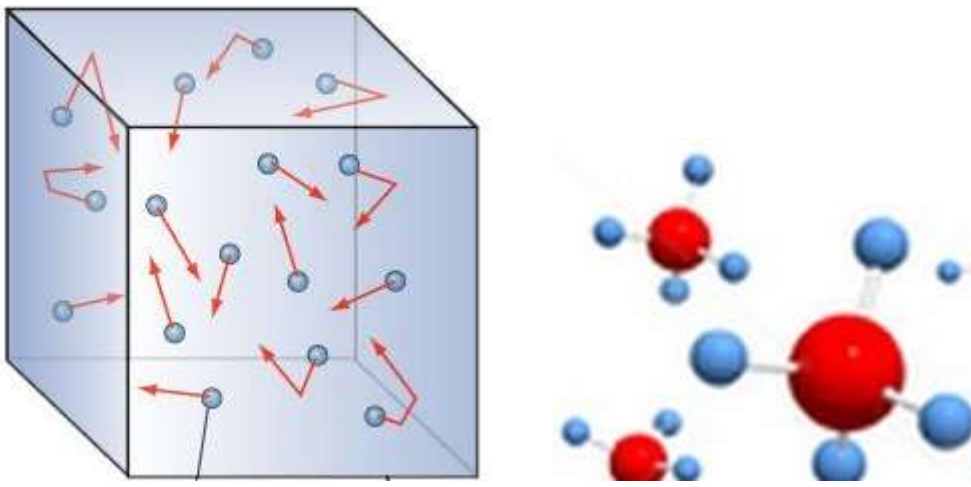


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Topic:

Second law and Entropy, Carnot's cycle & theorem, Entropy changes in reversible & irreversible processes, Entropy-temperature diagrams, Enthalpy, Gibbs, Helmholtz and Internal Energy functions.

2nd Law of Thermodynamics



Frequently Asked Questions & Numerical:

Solved Problems and Problems in exercise of Heat & Thermodynamics, Author A. B. Gupta, H.P Roy, Published by: Books & Allied Pvt. Ltd. (2018)

References:

i. *Heat & Thermodynamics, Author A. B. Gupta, H.P Roy, Published by: Books & Allied Pvt. Ltd. (2018)*

Link to Audio visual Lectures (e-Lectures) given by Distinguish Professors of Foreign Universities:

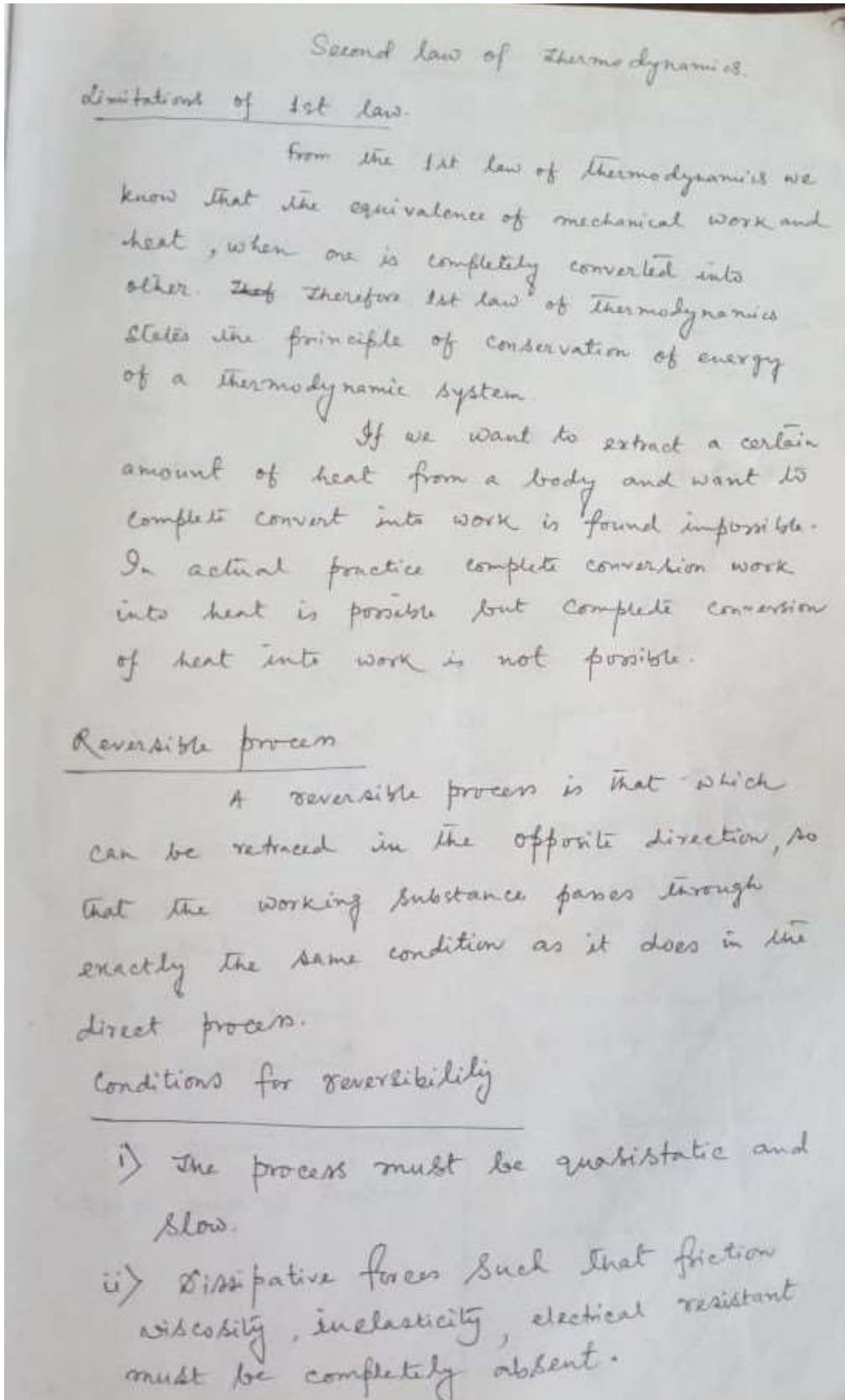
- i. https://www.youtube.com/watch?time_continue=2&v=i-bo0DoWqqA&feature=emb_title
- ii. <https://www.youtube.com/watch?v=RXo9SShMHvE>
- iii. https://www.youtube.com/watch?v=aDXBo0FtALA&list=PLwdnzlV3ogoVnCnIfjDHng_8biZSUEYtK



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A reversible engine can not be realised in practice.

i) We know that for a reversible engine $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

If $T_2 = 0$ then $Q_2 = 0$. Therefore, no heat can be rejected into sink.

ii) In reversible engine the working substance is an ideal gas. However, in practice no gas is ideal.

iii) For a reversible engine, the engine must be free from friction.

iv) For a reversible engine the states should be quasistatic i.e. the pressure and temperature of the working substance never differ appreciably from its surroundings at any stage of cycle.

These conditions are not maintained in practice. Therefore, a reversible engine can not be realised in practice.



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- Example
- (i) Slow ~~adiabatic~~ ^{isothermal} expansion of gas
 - (ii) Slow adiabatic compression of gas
 - (iii) Small extension and compression of spring.

Irreversible process

An irreversible process is that which cannot be retraced in the opposite direction so that the working substance does not pass through the same intermediate states through which it passes during the direct process.

- Example →
- (i) work done against friction.
 - (ii) Joule-Kelvin effect
 - (iii) Joule-Thomson effect
 - (iv) Joule expansion (free expansion) of a perfect gas.

Reversible process

- i) Reversible process is quasi-static
- ii) Reversible process is non-dissipative
- iii) In reversible process entropy remains constant

Irreversible process

- i) Irreversible process is non-static
- ii) Irreversible process is dissipative
- iii) In irreversible process entropy increases.

Entropy.

Entropy and its physical significance.

If a substance takes an amount of heat Q in a reversible process at a constant temperature T , then the ratio of heat and temperature $\frac{Q}{T}$ is called the increase in entropy of the substance i.e. ΔS .

$$\therefore \text{Change in entropy } (\Delta S) = \frac{Q}{T}$$
$$\text{or } \boxed{\Delta S = \int \frac{dq}{T}}$$

According to Statistical definition Entropy is the product of Boltzmann's constant (k) and natural log of thermodynamic probability W .

$$\text{i.e. } \boxed{S = k \ln W}$$

Physical Significance

i) Entropy is a state function.

ii) The entropy of the universe is continuously increasing.

iii) Like internal energy U and temperature T , the entropy S of a system is a physical property that can be measured.



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Kelvin - Planck statement of 2nd law:

"It is impossible to construct a device, operating a cycle, will take heat from a body and convert it completely into work without leaving any change anywhere."

Clausius Statement

"It is impossible to construct a device, operating in a cycle, will transfer heat from a cold body to hot body without expenditure of work by an external energy source."

Formulation of 2nd law of thermodynamics

If S_1 & S_2 be the nett entropies of a system in initial and final state,

$$\text{Change in entropy } (\Delta S) = S_2 - S_1 = \int_1^2 \frac{dq}{T}$$

In reversible path if the two states are infinitesimally close to each other then,

$$ds = \frac{dq}{T}$$

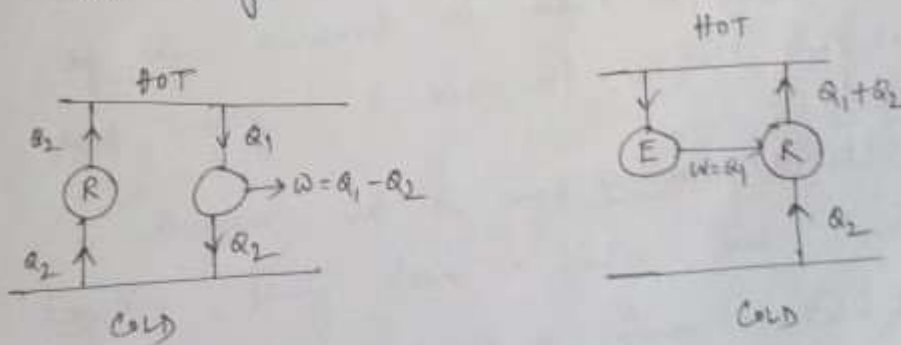
$$\boxed{dq = T ds}$$

→ mathematical expression of 2nd law.

Equivalence of Kelvin-Planck & Clausius Statement

Taking a refrigerator (R) which transfer an amount of heat Q_2 from a cold body to hot body without any internal supply of energy is against the Clausius Statement.

Now, we take an engine (E) working between same hot and cold bodies, takes Q_1 heat from hot body and convert $(Q_1 - Q_2)$ into work, finally rejects Q_2 into cold body. The engine alongs with Clausius law.



however, if the engine E & refrigerator R are combined together, they form a device that takes $Q_1 - Q_2$ heat from the hot & bod



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and converts all into work without giving up any amount of heat to the cold body. It is clearly against the Kelvin-Planck Statement.

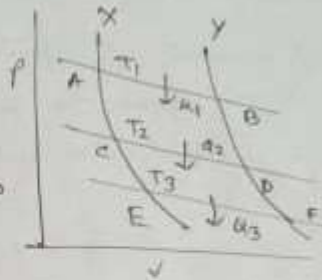
Similarly, let us suppose an engine E takes an amount of heat Q_1 from the hot body and converts completely into work $W = (Q_1)$ without giving up any heat to the cold body, against the Kelvin-Planck Statement.

A refrigerator R working between same two temperatures takes heat Q_2 from the cold body and converts work $W = (Q_1)$ giving up an amount of heat $Q_1 + Q_2$ to the hot body. R does not violate the law.

However, if R and E are combined together, they form a device - that transfers an amount of heat Q_2 from a cold body to hot body without any external energy source is against the Clausius-Statement. Thus the two statements are equivalent.

Concept of Entropy.

Let, x & y are two adiabatics on the P - V indicator diagram. & isothermals at temp T_1, T_2 & T_3 .



ABDC is Carnot's reversible cycle absorbs heat Q_1 at temp T_1 & rejects Q_2 at temp T_2

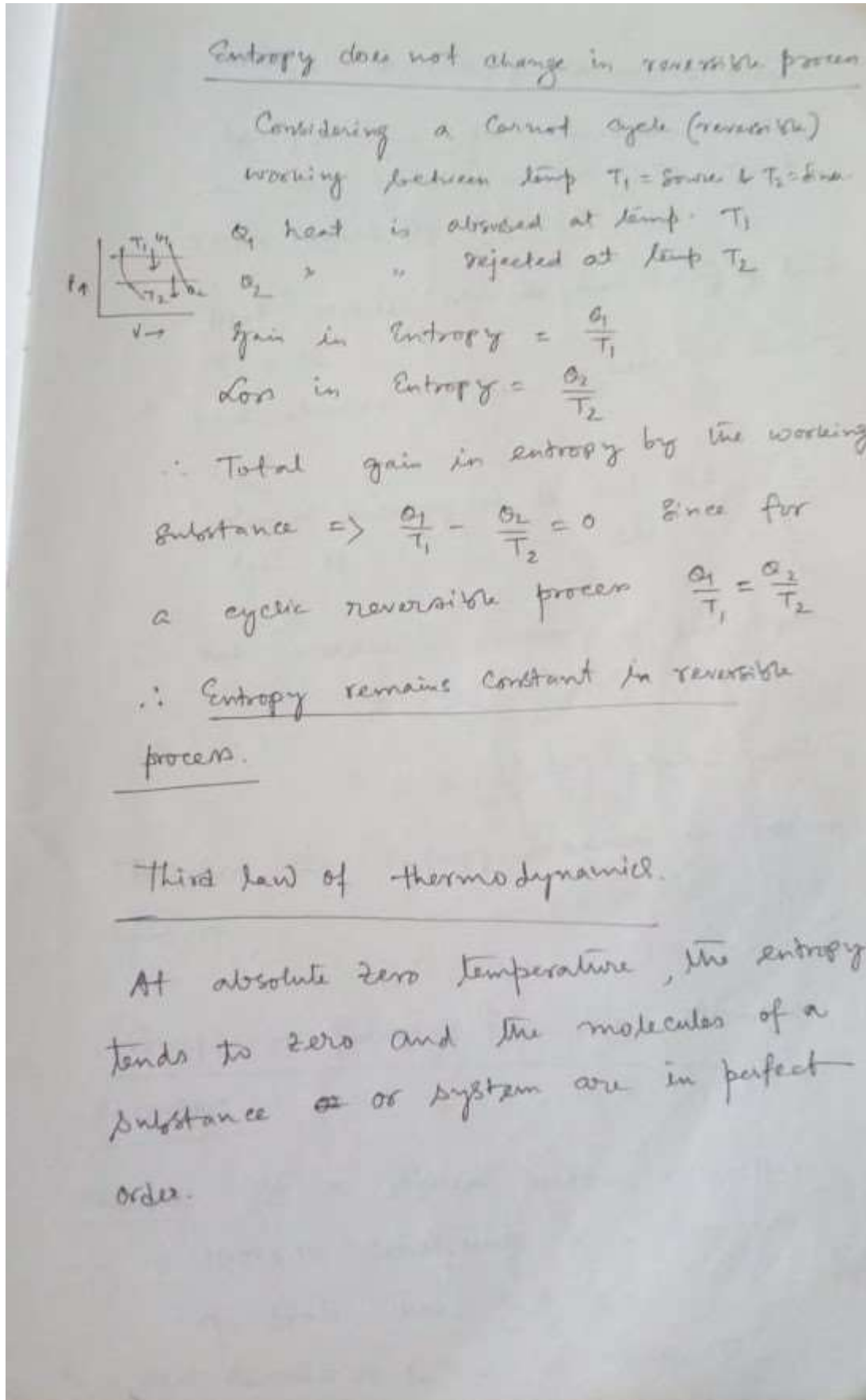
Thus, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ — (1)

Similarly CDFE represents the reversible cycle absorbs heat Q_2 at temp T_2 & rejects Q_3 at temp T_3

Thus $\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$ — (2)

From (1) & (2) $\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \dots = \text{Const}^n$

$\therefore \frac{Q}{T} = \text{Const}^n$
 Therefore, from one adiabatic to another adiabatic heat energy is either absorbed or rejected. The quantity Q is not Const^n & depends upon temp. T . However, $\frac{Q}{T}$ between two adiabatics is constant, called the change in entropy.





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Entropy increases in irreversible process

Let us think the conduction between the two bodies are at temp T_1 K & T_2 K, respectively ($T_1 > T_2$)

Heat rejected by the hot body at temp

$$T_1 = Q$$

Heat absorbed by the cold body at temp T_2

$$= Q$$

\therefore Loss of entropy of the hot body = $\frac{Q}{T_1}$
Gain of " " " " Cold " = $\frac{Q}{T_2}$

\therefore Net increase in entropy of the system

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

$$= Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = +ve \text{ quantity}$$

Therefore the entropy increases in irreversible process.

Concept of Entropy from the Clausius

Theorem?

Theorem: If a system performs a cyclic process consisting of a sequence of state then $\sum \frac{Q_i}{T_i} \leq 0$

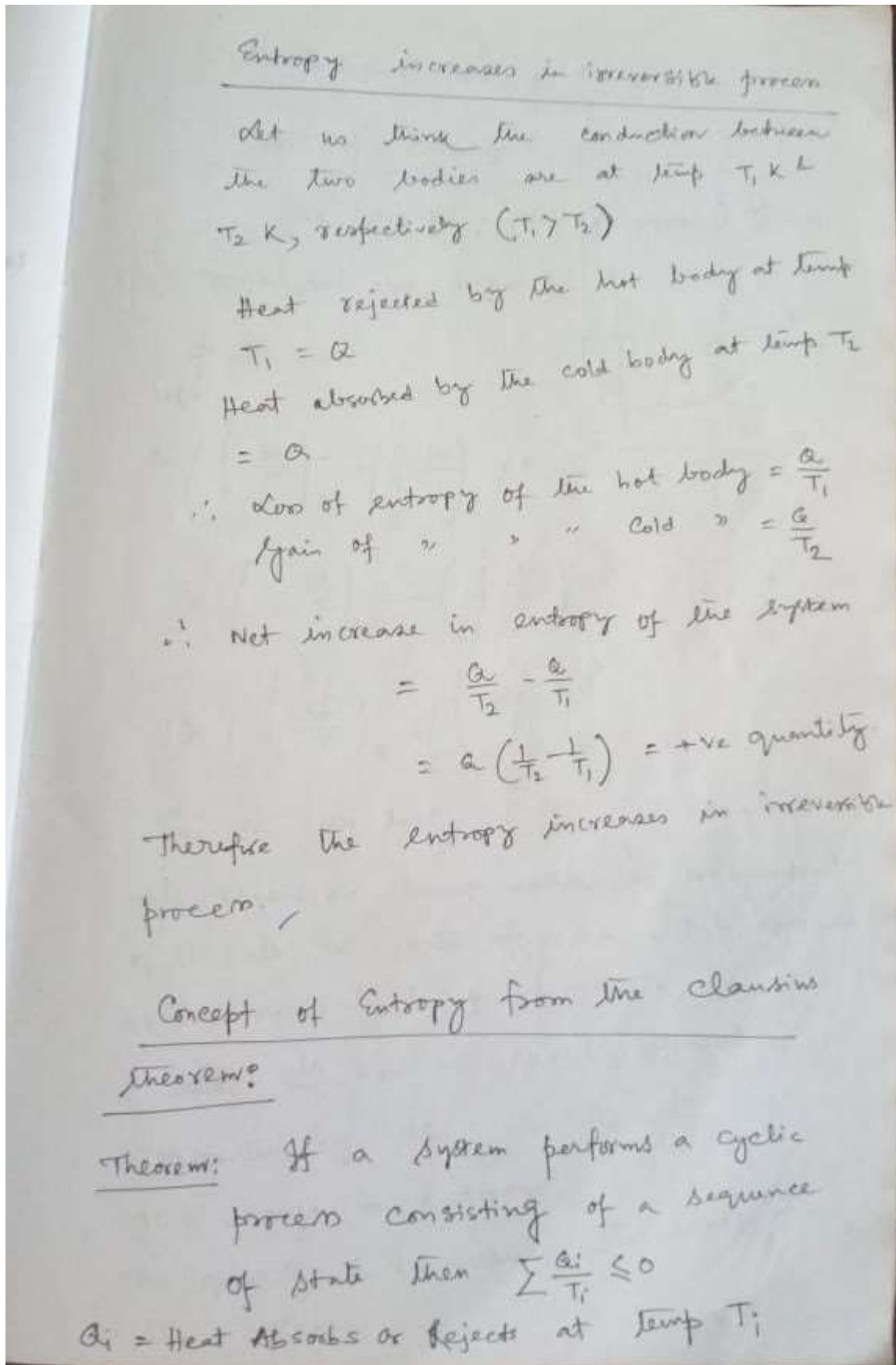
Q_i = Heat Absorbs or Rejects at Temp T_i



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An integral form of $\frac{dq}{T} \leq 0$

Concept of entropy

We have for a reversible cycle $\oint \frac{dq}{T} = 0$

from the indicator diagram.

$$\oint \frac{dq}{T} = 0$$

i x f y i

$$\Rightarrow \left(\int_i^f \frac{dq}{T} \right)_x + \left(\int_f^i \frac{dq}{T} \right)_y = 0$$

$$\Rightarrow \left(\int_i^f \frac{dq}{T} \right)_x = - \left(\int_f^i \frac{dq}{T} \right)_y$$

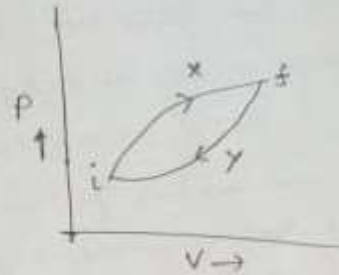
$$\Rightarrow \left(\int_i^f \frac{dq}{T} \right)_x = \left(\int_i^f \frac{dq}{T} \right)_y$$

So, we see that $\int_i^f \frac{dq}{T}$ is same for all reversible transformation is independent of path or state function. Only depends on the initial & final state

~~So~~ $\frac{dq}{T}$ is an exact differential represented by ds . $\therefore ds = \frac{dq}{T}$

ds = change in Entropy

The quantity s is called the entropy of the system.





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Entropy is a measure of disorder

If ω be the thermodynamic probability
 S be the Entropy & k is Boltzmann
Constant we know that $S = k \log \omega$

When complete and definite information
is known for all particles of a system
is said to be perfect order. The
~~the~~ uncertainty or loss of information
about the state of a system is called
disorder. The disorder is proportional to ω .

\therefore Entropy, being proportional to ω is
also related to disorder of the system.
Entropy is taken to be measure of
disorder. Every system tends to
proceed towards the state of maximum
disorder according to the law of
increase in entropy.