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Topics

Course	Topic Title
BSc	LYTIC AND LYSOGENIC CYCLE
BSc	BACTERIA GROWTH CURVE
BSc	NUCLEAR STRUCTURE AND FUNCTION
BSc	GRAM POSITIVE AND GRAM NEGATIVE CELL WALL

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BSc	GRAM POSITIVE AND GRAM NEGATIVE CELL WALL
BSc	GRAM STAINING AND ACID FAST STAINING
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APCCE LMS BIOTECHNOLOGY

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Topics

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BSc	CRYOPRESERVATION

Topics

Course	Topic Title
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BSc	CRYOPRESERVATION
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BSc	GENETICS GENE REGULATIONS
BSc	GENETICS INHERITANCE PATTERN
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BSc	23342 ISOTOPE INTRODUCTION
BSc	23343 STABLE ISOTOPES AND ITS MEASUREMENTS
BSc	23344 RADIOACTIVITY DECAY AND UNITS OF RADIOACTIVITY
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BSc	23372 DETERMINATION OF PH
BSc	23374 Introduction to Buffers
BSc	23375 Preparation of Buffers
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BSc	23327 Nucleus - Structure and Functions
BSc	23327 కేంద్రకం నిర్మాణం విధులు
BSc	23328 Chromatin and Chromosomes Structure Types and Functions
BSc	23328 క్రోమాటిన్ క్రోమోసోము నిర్మాణం రకాలు విధులు
BSc	11115 Locomotion in Protozoa

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Zoology	కేంద్రకం నిర్మాణం విధులు
Zoology	Chromatin and Chromosomes Structure Types and Functions
Zoology	క్రోమాటిన్ క్రోమోసోము నిర్మాణం రకాలు విధులు
Zoology	Locomotion in Protozoa
Zoology	ప్రోటోజోవాలో చలనం



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BSc	35554 CONCEPT OF ENTROPY
BSc	35553 కార్నో వలయం
BSc	35554 ఎంట్రోపి భావన

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Topics

Course	Topic Title
BSc	35553 CARNOT CYCLE
BSc	35554 CONCEPT OF ENTROPY
BSc	35553 కార్నో వలయం
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Mr. B. CHAKRAVARTHI	chakrizoologist@gmail.com	1482 min
Dr. N. SREENIVAS	zoonsreenivas4@gmail.com	1258 min
Dr. S. Ramakrishna	s7ramakrishna@gmail.com	1113 min
Sailaja Rani K.M.S	sailajakare@gmail.com	596 min
Sri B. Bhaskar Reddy	bhaskar.bandrevu@gmail.com	495 min
Dr.M. Pradeep	pradeep.m@gmail.com	482 min

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Carnot cycle

A heat engine converts thermal energy (heat) into mechanical energy (work). A steam engine is a heat engine in that the working fluid is steam. In the early 19th century, steam engines played a crucial role in the development of both industrial and transportation sectors. However, the theoretical calculation of efficiency of steam engine had not been yet explored. In the early 1820s *Nicolas Léonard Sadi Carnot*, a brilliant mechanical engineer in French Army, worked on steam engines. In 1824 he published a book *Reflections on the Motive Power of Fire*. In that book, he proposed a hypothetical and idealized steam engine that operating through different reversible thermodynamic processes and finally reaching to initial state. The cyclic process is named as *Carnot cycle*. The theoretical engine that operates on the Carnot cycle is called as *Carnot engine*. He was the first person to study the performance of heat engines. He explained clearly how and to what extent the work can be obtained from heat. Carnot is often described as the *Father of thermodynamics* due to his multiple scientific contributions to the thermodynamics.

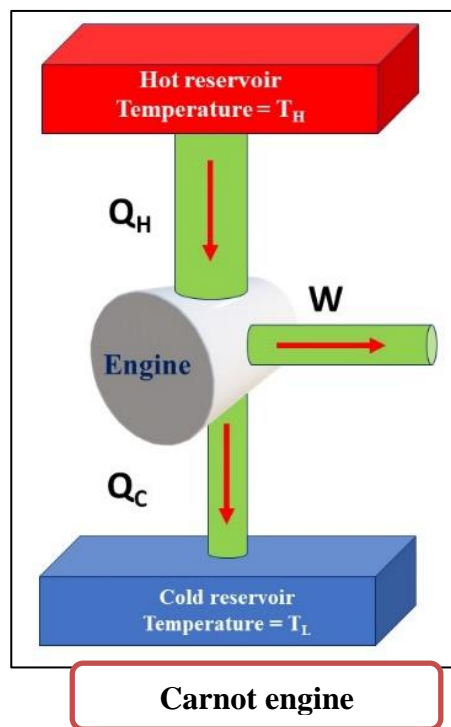
The design of basic model of Carnot engine was improved by Clapeyron. The ideas of Carnot were incorporated by Rudolf Clausius and William Thomson and proposed thermodynamic theories. The work of Carnot, Clapeyron, Clausius and Thomson led to the foundation of second law of thermodynamics and concept of entropy.

Construction of Carnot engine:

The Carnot engine consists of the following parts:

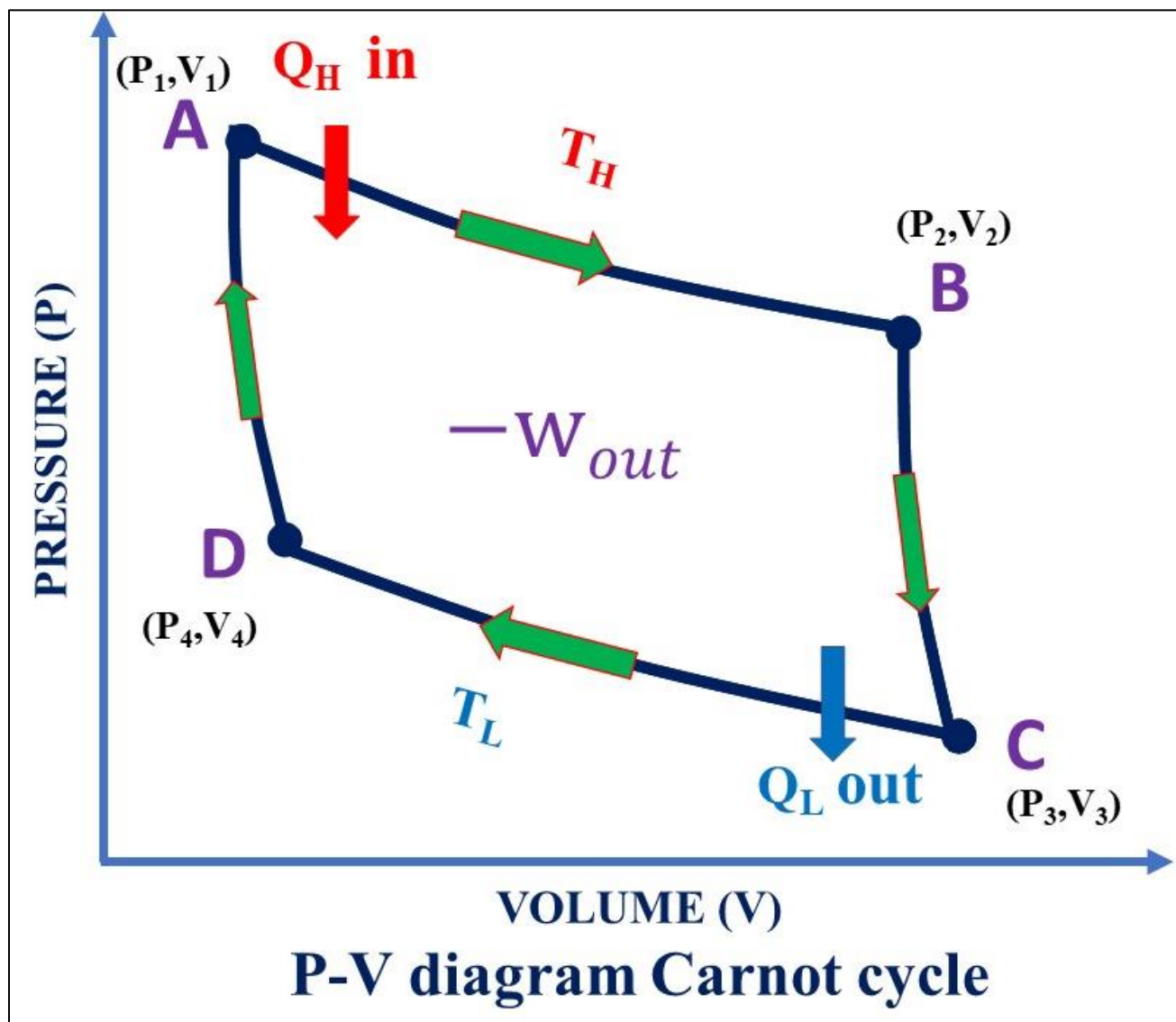
1. A cylinder containing one mole ideal gas having non-conducting side walls, non-conducting piston and conducting base.
2. A Hot reservoir (source) at temperature T_H
3. A Cold reservoir (sink) at temperature T_L
4. A non-conducting stand

Processes / Strokes in Carnot cycle:



The cycle involves two reversible isothermal processes and two reversible adiabatic processes. It consists of the following four hypothetical reversible thermodynamic processes taking place in a Carnot engine.

1. Reversible isothermal gas expansion
2. Reversible adiabatic gas expansion
3. Reversible isothermal gas compression process
4. Reversible adiabatic gas compression process

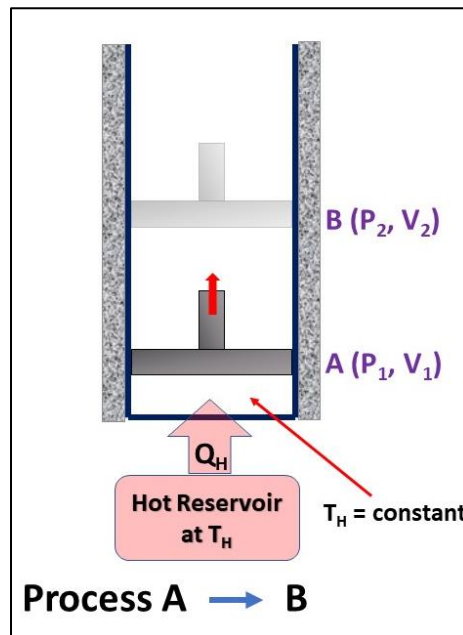


1. Reversible isothermal gas expansion (A → B):

The cylinder is placed on the hot reservoir (source) at temperature T_H and the gas in the cylinder is allowed to expand very slowly by removing weights on the piston and by supplying Q_H amount of heat. The volume of the gas increases from V_1 to V_2 . The state of the gas changes from initial state A (P_1, V_1, T_H) to intermediate state B (P_2, V_2, T_H). In the isothermal expansion of an ideal gas, the change in internal energy (ΔU) is zero.

According to first law of thermodynamics: $\Delta U = q + w$
 $\Rightarrow q = -w$

Here, $q = Q_H, w = w_1, Q_H = -w_1$



Work done by the system on surroundings in this stage = $-w_1 = 2.303RT \log (V_f / V_i)$

Here, $V_f = V_2, V_i = V_1, T = T_H$ $-w_1 = 2.303RT_H \log (V_2 / V_1)$

Heat absorbed by the system from surroundings = $Q_H = -w_1 = 2.303RT_H \log (V_2 / V_1) \dots (1)$

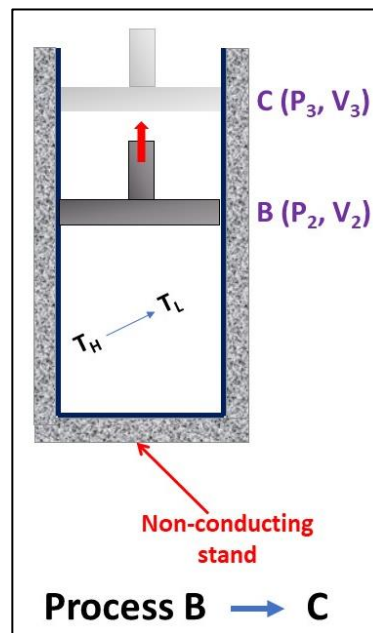
2. Reversible adiabatic gas expansion (B → C):

During this process, the gas containing cylinder is removed from the hot reservoir and is placed on the non-conducting stand. Then, the gas in the cylinder is expanded reversibly and adiabatically by removing weights on the piston. The volume of the gas increases from V_2 to V_3 , the pressure of the gas decreases from P_2 to P_3 and the temperature of the gas decreases from T_H to T_C . The state of the gas changes from first intermediate state (P_2, V_2, T_H) to second intermediate state B (P_3, V_3, T_C).

According to first law of thermodynamics: $\Delta U = q + w$
 $\Delta U = w \quad (\because q = 0)$

Molar heat capacity of one mole gas at constant volume

$$C_V = (\partial U / \partial T)$$

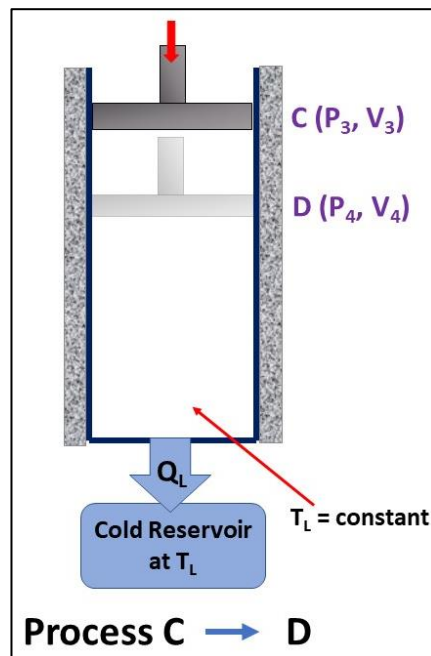


$$\Delta U = C_V \Delta T = C_V (T_f - T_i) = C_V (T_L - T_H)$$

Work done by the system on the surroundings in this stage = $w_2 = C_V (T_L - T_H)$ (2)

3. Reversible isothermal gas compression process (C → D):

During this process, the gas containing cylinder is removed from the non-conducting stand and is placed at cold reservoir (sink). Then, the gas in the cylinder is compressed reversibly and isothermally. The system releases heat to the sink and the work is done on the system by surroundings. In this process, the volume of the gas decreases from V_3 to V_4 , the pressure of the gas increases from P_3 to P_4 and the temperature is constant. The state of the gas changes from second intermediate state C (P_3, V_3, T_L) to third intermediate state D (P_4, V_4, T_L).



Work done on the system by the surroundings in this stage

$$= -w_3 = 2.303RT \log (V_4 / V_3)$$

Heat given out by the system to surroundings = $-Q_L = -w_3 = 2.303RT_L \log (V_4 / V_3)$(3)

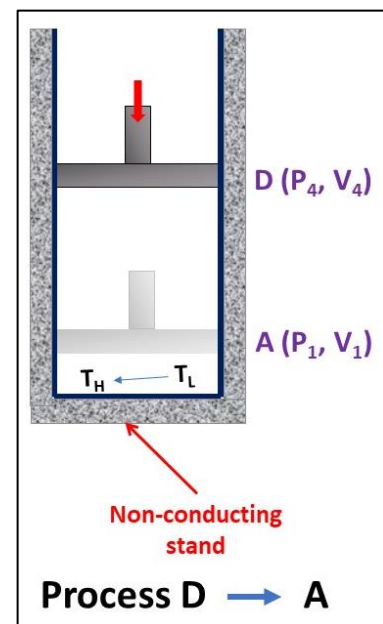
4. Reversible adiabatic gas compression process (D → A):

Finally, the cycle is completed by adiabatic compression process. During this process, the gas containing cylinder is removed from the cold reservoir and it is placed on non-conducting stand. Then, the gas in the cylinder is compressed reversibly and adiabatically. The volume of the gas decreases from V_4 to V_1 , the pressure of the gas increases from P_4 to P_1 and the temperature of the gas increases from T_L to T_H . The state of the gas changes from third intermediate state D (P_4, V_4, T_L) to the initial state A (P_1, V_1, T_H).

$$\Delta U = w \quad (\because q = 0)$$

Molar heat capacity of one mole gas at constant volume

$$C_V = (\partial U / \partial T)$$



$$\Delta U = C_v \Delta T = C_v (T_f - T_i) = C_v (T_H - T_L)$$

Work done on the system by the surroundings in this stage = $w_4 = C_v (T_H - T_L)$(4)

The net heat absorbed by the system in this cyclic process = $Q = Q_H + (-Q_L)$

$$Q = 2.303RT_H \log (V_2 / V_1) + 2.303RT_C \log (V_4 / V_3) \dots\dots(5)$$

For adiabatic changes for points B and C $T_H V_2^{\gamma-1} = T_L V_3^{\gamma-1} \dots\dots(6)$

For adiabatic changes for points A and D: $T_H V_1^{\gamma-1} = T_L V_4^{\gamma-1} \dots\dots(7)$

From the Eq. 6 & 7 $\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} \Rightarrow \frac{V_1}{V_2} = \frac{V_4}{V_3} \dots\dots(8)$

From the Eq. 5 & 8 $Q = 2.303RT_H \log (V_2 / V_1) + 2.303RT_L \log (V_1 / V_2)$

$$Q = 2.303RT_H \log (V_2 / V_1) - 2.303RT_L \log (V_2 / V_1)$$

Net heat absorbed by the system (Q) = $2.303R (T_H - T_L) \log (V_2 / V_1) \dots\dots(9)$

Net work done by the gas = $w = -w_1 - w_2 + w_3 + w_4$

$$w = 2.303RT_H \log (V_2 / V_1) + C_v (T_L - T_H) + 2.303RT_L \log (V_2 / V_1) + C_v (T_H - T_L)$$

$$w = 2.303RT_H \log (V_2 / V_1) - 2.303RT_L \log (V_2 / V_1)$$

$$w = 2.303R(T_H - T_L) \log (V_2 / V_1) \dots\dots(10)$$

Efficiency (η):

The efficiency of the Carnot engine is defined as the ratio of net work done by the heat engine to the net heat absorbed by the heat engine

$$\text{Efficiency } (\eta) = \frac{\text{Net work done by Carnot engine}}{\text{Heat absorbed by Carnot engine}} = \frac{w}{Q_H} = \frac{Q_H - Q_L}{Q_H} = \frac{T_H - T_L}{T_H} \dots\dots(11)$$

$$T_H > T_L \Rightarrow T_H - T_L > 0 \text{ \& } T_H - T_L > T_H$$

$$\Rightarrow \frac{T_H - T_L}{T_H} > 0 \ \& \ \frac{T_H - T_L}{T_H} > 1$$

- The efficiency of Carnot engine is always less than 1. It ranges between 0 to 1
- The efficiency of engine depends on the temperature difference between source and sink.
- No heat engine which has efficiency equal to 1 has yet been constructed. Theoretically it is possible when the sink temperature $T_C = 0 \text{ K}$
- In practice, the efficiency of steam engine even less than that given by the Eq.1.1, since all the processes in steam engine are irreversible.

Carnot Theorem:

1. It is impossible to construct a heat engine (irreversible engine) which is more efficient than a Carnot engine (reversible engine) when operating between the same two temperatures

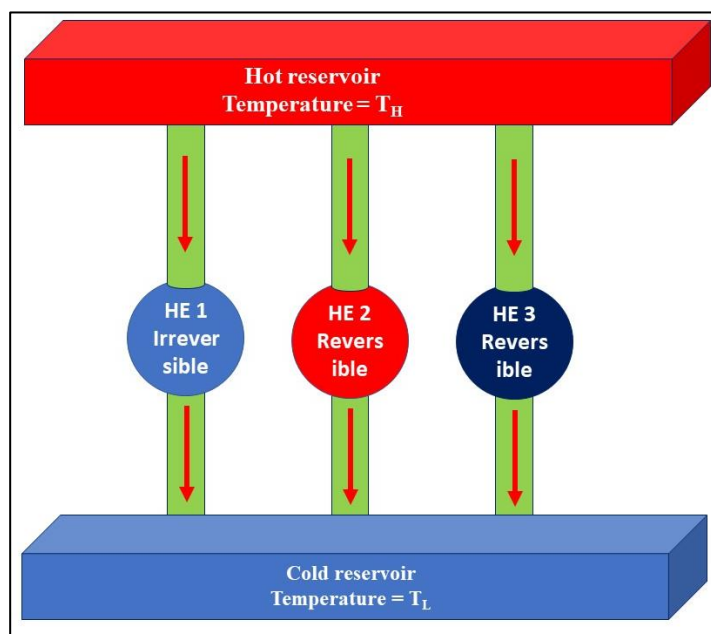
$$\eta_{\text{Carnot engine}} > \eta_{\text{Heat engine}}$$

2. The efficiency of all Carnot engines (reversible engines) operating between the same two temperatures is same

$$\eta_1 < \eta_2$$

$$\eta_1 < \eta_3$$

$$\eta_2 = \eta_3$$



Reference books: Principles of Physical Chemistry by Puri, Sharma and Pathania

Physical Chemistry by Peter Atkins and Julio De Paula

Reading Materials: https://en.wikipedia.org/wiki/Carnot_cycle

<https://www.britannica.com/science/Carnot-cycle>

Concept of Entropy

Let us take a Carnot cycle in which Q_H amount of heat is absorbed by the system from the hot reservoir at temperature T_H and Q_L amount of heat is evolved by the system to cold reservoir at temperature T_L .

The efficiency of the Carnot engine operates on the above described Carnot cycle:

$$\begin{aligned} \text{Efficiency } (\eta) &= \frac{Q_H - Q_L}{Q_H} = \frac{T_H - T_L}{T_H} \\ \Rightarrow 1 - \frac{Q_L}{Q_H} &= 1 - \frac{T_L}{T_H} \\ \Rightarrow \frac{Q_L}{Q_H} &= \frac{T_L}{T_H} \\ \Rightarrow \frac{Q_L}{T_L} &= \frac{Q_H}{T_H} \quad \dots\dots(1) \end{aligned}$$

When we give positive sign to heat absorbed (Q_H) and negative sign to heat evolved ($-Q_L$)

$$\begin{aligned} \frac{-Q_L}{T_L} &= \frac{Q_H}{T_H} \\ \Rightarrow \frac{Q_H}{T_H} + \frac{Q_L}{T_L} &= 0 \quad \dots\dots(2) \end{aligned}$$

The general forms of Eq. 1 & Eq. 2 are

$$\frac{q_{rev}}{T} = \text{constant} \quad \dots\dots(3)$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad \dots\dots(4)$$

Here q_{rev} , q_1 , and q_2 are the amount of heat exchanged in a reversible process at a temperature T , T_1 , and T_2 respectively

Any cyclic process can be shown to consist of series infinity number of Carnot cycles. Consider a cyclic process consists of processes of change of state 'A' to state 'B' and change of state 'B' to state 'A' reversibly with different paths. The cyclic path ABA can be shown with consisting of infinity number of Carnot cycles as shown in the below figure

From Eq. (4) for each Carnot cycle

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

The sum of all the $\frac{q}{T}$ terms of the infinity number of Carnot cycles on the ABA curve is zero,

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

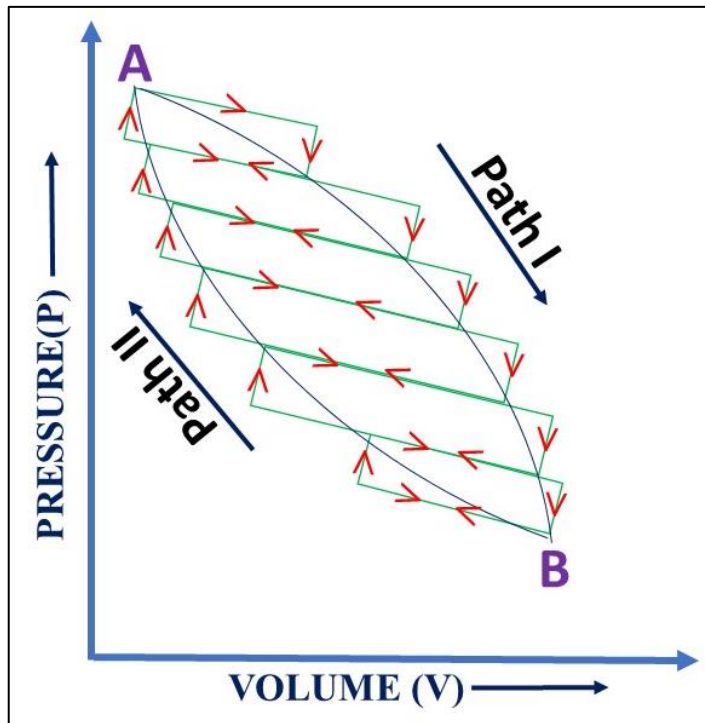
When the changes are infinitesimal $q = dq$,

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

$$\Rightarrow \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0$$

$$\Rightarrow \int_A^B \frac{dq}{T} = - \int_B^A \frac{dq}{T}$$

$$\Rightarrow \int_A^B \frac{dq}{T} (\text{path I}) = \int_A^B \frac{dq}{T} (\text{path II}) \dots\dots\dots(5)$$



From the Eq. 5 the quantity $\int_A^B \frac{dq}{T}$ is a definite quantity and independent of the path of the process and depends only on initial and final states of the process. The quantity is called as entropy (S).

If the entropy of the system at initial state is S_A and at final state is S_B then the change in entropy

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}$$

For infinitesimally small change in entropy $dS = \frac{dq}{T} \dots\dots\dots(6)$

For a finite change in entropy $dS = \Delta S$, $dq = q$, then $\Delta S = \frac{q}{T} \dots\dots\dots(7)$

Definition of entropy (S):

Unavailable energy per unit temperature in a system is defined as entropy

$$\text{Entropy (S)} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

Definition of entropy change (ΔS):

Heat transferred per unit temperature in a reversible process is called as entropy change

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

Units of entropy:

It has the dimension of energy divided by temperature.

Entropy: J K^{-1} (Joules per degree kelvin)

Specific entropy: $\text{J kg}^{-1}\text{K}^{-1}$

Molar entropy: $\text{J mol}^{-1}\text{K}^{-1}$

Entropy change in different processes:**Isothermal expansion or compression of gas:**

For the expansion or compression of an **ideal gas** from an initial volume V_i and pressure P_i to final volume V_f and pressure P_f at a constant temperature T , the change in entropy

$$\Delta S = 2.303 n R \log \left(\frac{V_f}{V_i} \right) = 2.303 n R \log \left(\frac{P_i}{P_f} \right)$$

Cooling and heating:

For heating and cooling of **any system (gas, liquid or solid)** from an initial temperature T_i to final temperature T_f .

Isobaric process (pressure is constant): $\Delta S = 2.303 n C_p \log \left(\frac{T_f}{T_i} \right)$

Isochoric process (volume is constant): $\Delta S = 2.303 n C_v \log \left(\frac{T_f}{T_i} \right)$

The above equations are valid when there is no change in molar heat capacity and no phase transition take place in this temperature interval

Change in entropy when T & P are the two variables:

$$\Delta S = 2.303 n C_v \log \left(\frac{T_f}{T_i} \right) + 2.303 n R \log \left(\frac{P_i}{P_f} \right)$$

Change in entropy when T & V are the two variables

$$\Delta S = 2.303 n C_p \log \left(\frac{T_f}{T_i} \right) + 2.303 n R \log \left(\frac{V_f}{V_i} \right)$$

Phase transitions:

Reversible phase transitions occur at constant temperature and pressure

Change in entropy = $\frac{\text{enthalpy change for the transition}}{\text{temperature at which transition occurs}}$

$$\text{Entropy of fusion} \quad \Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}$$

(ΔH_{fus} = enthalpy of fusion, T_m = melting point)

$$\text{Entropy of vaporization} \quad \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

(ΔH_{vap} = enthalpy of vaporization, T_m = boiling point)

Physical significance of entropy:

Entropy is a real physical quantity and it is a state function like pressure, temperature, volume, internal energy and enthalpy.

1. Entropy and unavailable energy:

According to the second law of thermodynamics, the conversion of whole internal energy of a system into useful work is not possible. A portion of the energy which is used for doing useful work is called **available energy** and the remaining portion of energy is called **unavailable energy**. Entropy is a measure of this unavailable energy per unit temperature. The unavailable energy is used for structural changes in system

$$\text{Entropy (S)} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

2. Entropy and disorder:

Entropy is a measure of the disorder or randomness in the system. All spontaneous processes accompanied with increase in randomness and increase in entropy.

E.g. mixing of gases increases both disorder and entropy

3. Entropy and probability:

In nature, more disordered (more entropic) states are more probable than less disordered (less entropic) states. So, entropy and thermodynamic probability are closely related

Boltzmann entropy equation: **$S = k \ln W$**

(W = thermodynamic probability, k = Boltzmann constant)

$$W = \frac{\text{Probability of actual state}}{\text{Probability of complete ordered state}}$$

For a solid at 0 K (ideal solid) $W = 1 \Rightarrow S_0 = 0$

4. Entropy and spontaneity:

All the spontaneous processes cause an increase in entropy of the universe ($\Delta S_{\text{univ}} > 0$)

All nonspontaneous processes cause a decrease in entropy of the universe ($\Delta S_{\text{univ}} < 0$)

All reversible processes cannot change entropy of the universe ($\Delta S_{\text{univ}} = 0$)

5. Entropy and energy dispersal:

Entropy is a measure of energy dispersal or spread at a specific temperature. Entropy measures the number of microstates. The increase in energy dispersal in a system increases entropy due to increase in number of microstates.

Features of entropy:

- It is an extensive property and a state function
- At equilibrium (reversible process) $\Delta S = 0$
- For a cyclic process $\Delta S = 0$
- For a natural process (irreversible process) $\Delta S > 0$ i.e. in spontaneous process entropy increases (The second law of thermodynamics)
- For an isolated system such as universe $\Delta S > 0$ i.e. entropy increases
- For an adiabatic process $\Delta S = 0$
- For perfect crystalline solids (ideal solids) $S = 0$ (The third law of thermodynamics)
- Entropy approaches zero ($S \rightarrow 0$) as temperature approaches zero ($T \rightarrow 0$) (The third law of thermodynamics)

Model questions:

1. Write a short note on entropy
2. Explain concept and physical significance of entropy
3. Define the 2nd and 3rd law of thermodynamics in terms of entropy

Reference books: Principles of Physical Chemistry by Puri, Sharma and Pathania

Physical Chemistry by Peter Atkins and Julio De Paula

Reading Materials: <https://en.wikipedia.org/wiki/Entropy>

<https://edu.rsc.org/feature/what-is-entropy/2020274.article>

<http://www.scholarpedia.org/article/Entropyv>

APCCE-LMS-CHEMISTRY

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