



Discipline Course-I
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Lesson: Entropy I
Lesson Developer: Dr. Ajay Kumar
College/ Department: Deshbandhu College, Physics
Department,
University of Delhi

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Objectives

In this chapter, you will be able to understand about;

- ✓ The definitions of Entropy
- ✓ The significance of Entropy
- ✓ The mathematical formulation of Entropy
- ✓ The expressions for change in entropy of a system undergoing reversible/irreversible changes
- ✓ The Clausius inequality
- ✓ The representation of Carnot cycle on T-S diagram

8.1 Introduction

In the previous chapters, we have familiarized ourselves with various thermodynamic processes and laws. The first law of thermodynamics governs the transformation of heat into work. However, this law does not make any constraint on the direction of heat flow. Generally, in the absence of any external agency, the transfer of heat from a hotter body to a cooler one is a physically possible process, however the reverse is not possible. In a refrigerator, the heat is transferred from cooler components to hotter one but with the help of external electrical energy. These observations are contained in the second law of thermodynamics which governs the direction of transfer of thermal energy. The concept of entropy could be understood as the manifestation of this second law, according to which the entropy of an isolated system always increases or remains constant. Thus, we can interpret entropy as a measure of the tendency of favorable occurrence of a process such as a chemical reaction in a particular direction. It has been found that all the natural processes progress in the direction of increase in entropy and hence, it implies that the **arrow of entropy** has the same direction as that of **arrow of time** (as time always progresses).

8.2 Clausius theorem

It is a fundamental theorem which demonstrates the existence of an important state function, value of which remains the same in bringing reversibly a thermodynamic system from one state to another by adiabatic means.

8.2.1 Statement

According to the Clausius theorem, the integral of the ratio of heat transferred and temperature (at which the heat is transferred) in a reversible thermodynamic cyclic process always comes out to be zero. Mathematically,

$$\oint_R \frac{dQ}{T} = 0 \quad (8.1)$$

where T is the temperature at which the heat dQ is transferred. The integration is taken over the complete cycle.

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8.2.2 Proof

To deduce Clausius theorem, we will start from a concept of replacement of a thermodynamic process into consecutive sub portions of isothermal and adiabatic processes. For that let us consider a process in which a thermodynamic system is taken from an initial state i to a final state f reversibly. This process can easily be represented as a smooth curve on a generalized work diagram as shown in figure 8.1.

The dashed lines through initial and final points represent the portions of adiabatic processes. Now a smooth curve ab representing a portion of an isothermal process can be drawn in such a manner that the area under smooth curve if is equal to the area under zigzag curve $iabf$, consisting of portions of two adiabatic and one isothermal processes. Obviously, the work done in following both the paths will be the same i.e.

$$W_{if} = W_{iabf}$$

Now, from the first law of thermodynamics:

$$dQ = dU + dW$$

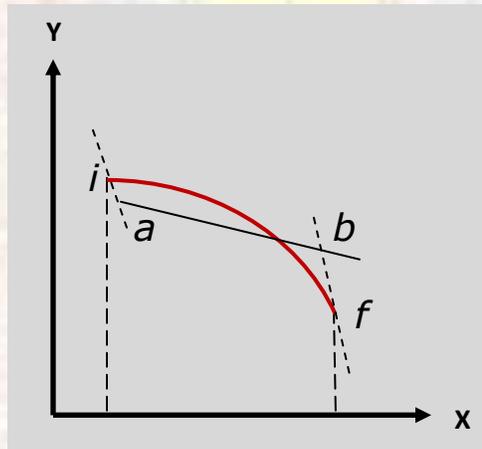


Figure 8.1: Generalized work diagram where $i-f$ represents any reversible thermodynamic process, ia and bf are adiabatic segments, ab is isothermal process. X and Y represent generalized displacement and force respectively.

For process $i-f$,

$$Q_{if} = U_f - U_i + W_{if}$$

And for process $iabf$,

$$Q_{iabf} = U_f - U_i + W_{iabf}$$

We, therefore, may write,

$$Q_{if} = Q_{iabf}$$

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The processes ia and bf are portions of adiabatic, therefore heat transferred during these processes is zero and hence

$$Q_{if} = Q_{ab}$$

From above discussion, it may be concluded that

"A reversible process in which temperature may change in any manner, can be replaced by a reversible zigzag path consisting of an adiabatic process followed by an isothermal process followed by an adiabatic process with the condition that the heat transferred during the isothermal process is the same as that during the original process".

Now, let us consider a smooth closed curve on the generalized work diagram as shown in figure 8.2. With the fact that no two adiabatic lines on a work diagram can intersect each other, a number of such line can be drawn intersecting the closed curve into a large number of stripes. Let us draw a zigzag closed path $abcd$ consisting of alternate adiabatic and isothermal segments in such a manner that the heat transferred during the isothermal segments is the same as that due to the small portion of the original cycle. Now, if the heat absorbed during the isothermal segment ab at temperature T_1 is Q_1 and heat rejected during the isothermal process cd at temperature T_2 is Q_2 , then, since closed curve $abcd$ forms a Carnot cycle, we may write

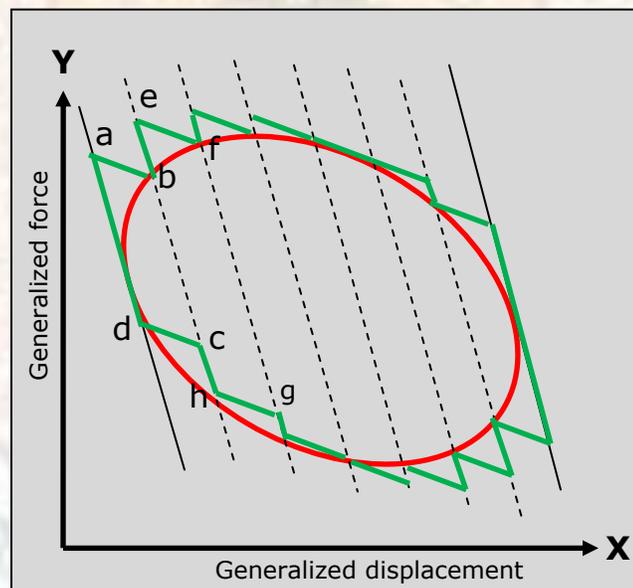


Figure 8.2: Generalized work diagram where a closed smooth curve (red) has been divided into a large number of adiabatic stripes connected by small isothermal portions.

$$\frac{|Q_1|}{T_1} = \frac{|Q_2|}{T_2}$$

or

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$$\frac{Q_1}{T_1} = \frac{-Q_2}{T_2}$$

Here positive and negative signs are used for heat absorbed and heat rejected respectively. Above equation can be written as:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

The zigzag path *efgh* also represents a Carnot cycle in which heat Q_3 is absorbed at temperature T_3 and Q_4 amount of heat is rejected at temperature T_4 . For this cycle we may write

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$$

Similar equations may be written for each pair of isothermal curve bounded by two adiabatic curves intersecting the original closed curve. On adding all the equations, we get

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} \dots \dots \dots = 0 \quad (8.2)$$

Since no heat is transferred during the adiabatic portions of these Carnot cycles, we may express above equation as

$$\sum_n \frac{Q_n}{T_n} = 0$$

Here the summation is taken over the entire zigzag path consisting of n Carnot cycles.

The original closed curve, in this way, may be divided into a large number of adiabatic stripes bounded with small isothermal curves such that the zigzag path made by Carnot cycles approximates the original closed curve. Then the ratio dQ/T for an infinitesimal isothermal bounded by two adjacent adiabatic curves is equal to the ratio dQ/T for infinitesimal portion of the original closed curve bounded by the same two adiabatic curves. In this limit, therefore, we may write

$$\oint_R \frac{dQ}{T} = 0$$

Where \oint represent the integration taken over the complete cycle. It should be noted here that above result, known as **Clausius theorem**, is true only for reversible cycles.

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Consider points i and f on the generalized work diagram representing initial and final equilibrium states of any thermodynamic system [Figure 8.3]. As i and f are equilibrium states, the system can be taken from state i to f along any number of reversible paths. Suppose the system is taken from i to f by following a reversible path R_1 and back to i along another reversible path R_2 .

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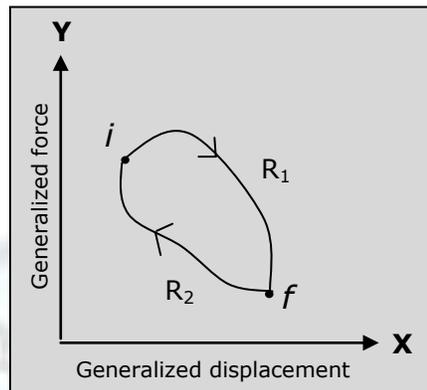


Figure 8.3: Generalized work diagram where i and f represents two equilibrium states of any thermodynamic system, R_1 and R_2 are two reversible paths connecting the two states.

It is clear from figure 8.3 that paths R_1 and R_2 form a closed reversible cycle. From Clausius theorem, we may write

$$\oint_{R_1 R_2} \frac{dQ}{T} = 0$$

or

$$\int_{i, R_1}^f \frac{dQ}{T} + \int_{f, R_2}^i \frac{dQ}{T} = 0$$

Or

$$\int_{i, R_1}^f \frac{dQ}{T} = - \int_{f, R_2}^i \frac{dQ}{T}$$

Since R_2 is a reversible path, we may write

$$\int_{i, R_1}^f \frac{dQ}{T} = \int_{i, R_2}^f \frac{dQ}{T} \quad (8.3)$$

8.3.1 Definition of entropy

In above discussion, the reversible paths R_1 and R_2 were chosen arbitrarily and they represent any two reversible paths connecting points i and f . Equation (8.3), therefore, expresses the fact that $\int_R \frac{dQ}{T}$ is independent of the reversible path along which the system is taken from i to f . It indicates, therefore, the existence of a thermodynamic function whose value at final state minus its value at initial state is equal to the $\int_R \frac{dQ}{T}$. In 1865, **Rudolf Clausius** coined the name entropy for this state function and represented it by ' S '. If S_f and

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S_i be the entropies of final and initial states of a thermodynamic system, then the change in entropy in taking the system from state i to f is given by;

$$\Delta S = S_f - S_i = \int_{i,R}^f \frac{dQ}{T} \quad (8.4)$$

If the points i and f of the system be infinitesimally near, then the change in entropy is given by;

$$dS = \frac{dQ}{T} \quad (8.5)$$

Where, dQ is the small amount of heat transferred (absorbed or rejected) by the system at temperature T . Equation (8.5) if written as $dQ = TdS$, is known as the mathematical form of **second law of thermodynamics**, according to which all the natural processes (physical, chemical etc.) in the universe progress in such a way that the entropy of the universe always increases.

Did you know?

- The change in entropy of a system is path independent; however, the heat entering (or) leaving the system is path dependent.
- The change in entropy dS , being a differential of an actual function is an exact differential whereas the quantities like heat dQ and work dW are inexact one.

8.3.2 Unit of entropy

The unit of entropy is **Joules/Kelvin** and **Erg/Kelvin** (or **Calorie/Kelvin**) in SI and CGS systems respectively.

8.3.3 Physical significance

To understand the importance of entropy, let us consider the phenomenon of melting of a solid at atmospheric pressure. When latent heat is supplied to the solid, it change it into liquid at constant temperature. In the liquid state, the molecules are randomly distributed and can move independently in the whole volume of the liquid. However, in a solid, the constituent molecules form a rigid structure in a well-organized manner or ordering of molecules *i.e.* a solid is capable of supporting itself. So, we can say that the liquid is in a state of **disorder**, relative to its solid state. It follows from the above discussion that; an increase in the entropy of a system can be interpreted as an **increase in the disorder** of the system.

Historical

After performing extensive studies, Rudolf Clausius, a German physicist, set forth the concept that whenever work is done by an irreversible process, there always exists an inherent heat loss due to friction or some other means. This unavoidable heat loss is irreversible *i.e.* it can not be utilized. He put forth an argument about this small heat loss across the system's

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boundary during any irreversible process. In 1865, Clausius gave the name **entropy** to this irreversible heat loss.

"I propose to name the quantity S the entropy of the system, after the Greek word [τροπή trope], the transformation. I have deliberately chosen the word entropy to be as similar as possible to the word energy: the two quantities to be named by these words are so closely related in physical significance that a certain similarity in their names appears to be appropriate".



Rudolf Clausius
(Image taken from Wikipedia)

8.4 Clausius inequality

According to Clausius theorem, for a **reversible** cycle, the ratio of heat transferred (absorbed/rejected) and the temperature at which heat is transferred equals zero when integrated for the entire cycle i.e. $\oint_R \frac{dQ}{T} = 0$

However, the natural processes possess a tendency to occur irreversibly. So, it is interesting to find out the value of above integral for an irreversible process. For that, let us consider a system of a reversible engine (R) and irreversible engine (I) coupled together [Figure 8.4].

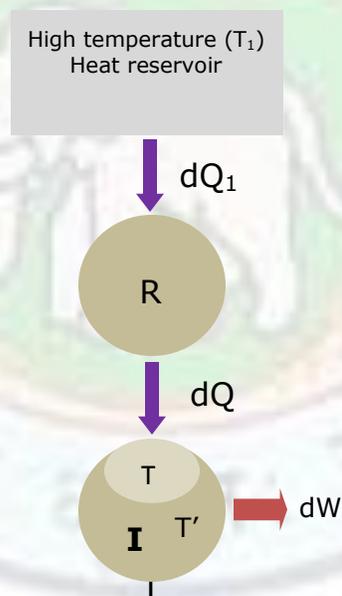


Figure 8.4: Combination of a reversible engine (R) and irreversible engine (I) performing an irreversible cycle. Engine R takes heat dQ_1 from high temperature (T_1) reservoir and transfers small heat dQ to engine I at constant temperature T .

Sup| and rejects heat dQ to the engine I at temperature T . After taking heat dQ , engine I performs a small work dW irreversibly. Clearly, combined system of engines R and I perform an irreversible cycle. Now, the heat dQ_1 is absorbed by engine R at constant T_1)

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temperature, the work done in the combined irreversible cycle can be found out using first law of thermodynamics *i.e.*

$$dQ = dU + dW$$

As heat is transferred at constant temperature, then, obviously, there will be no change in internal energy. So,

$$dQ = dW$$

And for complete cycle;

$$\oint dQ_1 = dW$$

Now, we have three possibilities;

1. $\oint dQ_1 = 0$; which means that engine I and its surroundings restore their original state at the end of the cycle but it is contrary to the irreversibility of engine I, therefore it follows that; $\oint dQ_1 \neq 0$
2. $\oint dQ_1 > 0$; which means that the net work done by the combined system is positive. However, according to the Kelvin-Planck's statement of the second law of thermodynamics, it is not possible to extract positive work by a combined system of engines which takes heat from a single reservoir.
3. $\oint dQ_1 < 0$; which is the only possibility.

Now, from the definition of thermodynamic scale of temperature, we may write,

$$\frac{|dQ_1|}{|dQ|} = \frac{T_1}{T}$$

Or

$$\frac{dQ_1}{T_1} = \frac{-dQ}{T}$$

Integration around the cycle of above equation yields;

$$\oint_R \frac{dQ_1}{T_1} = \oint_R \frac{-dQ}{T}$$

or

$$\frac{1}{T_1} \oint_R dQ_1 = - \oint_R \frac{dQ}{T} \text{ (Because } T_1 \text{ is constant and positive)}$$

The heat rejected by engine R ($-dQ_R$) is absorbed by engine I *i.e.* $-dQ_R = dQ_I$, we may write;

$$\oint \frac{dQ_I}{T} = \frac{1}{T_1} \oint_R dQ_1$$

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$$\oint \frac{dQ}{T} = \frac{1}{T_1} \oint dQ_1$$

But $\oint_R dQ_1 < 0$; so,

$$\oint \frac{dQ}{T} < 0, \text{ (for irreversible cycle)} \quad (8.6)$$

So, the ratio of heat transferred and temperature *at which heat is transferred* in an internally irreversible thermodynamic cycle is always less than zero. This result is known as Clausius inequality.

8.5 T-S diagram

A diagram in which temperature T is plotted (on X-axis) against entropy S (on Y-axis) is called as T-S diagram. To understand the interpretation of T-S diagram, let us consider that a small amount of heat (dQ) is absorbed at temperature T by a system during an infinitesimal portion of a reversible process. Then from the definition of entropy, we may write;

$$dQ = TdS \quad (8.7)$$

The total heat absorbed during the whole process can be calculated by integrating above equation i.e.

$$Q = \int_i^f dQ = \int_i^f TdS$$

Now, the quantity on the right hand side can be interpreted as the area under the curve on a T-S diagram and is equals to the total amount of heat absorbed during the process.

Interesting fact

In above discussion, it seems that the area under curve on a T-S diagram represents the total heat absorbed during the complete process but, according to the first law of thermodynamics;

$$Q = \int_i^f dQ = W$$

(because heat is transferred at constant temperature and hence $dU = 0$)

So, the area under the curve on a T-S diagram represents the amount of heat converted into the work.

We know that a Carnot cycle consists of two adiabatic and two isothermal processes. Adiabatic and isothermal processes appear on the T-S diagram in the form of a vertical and

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horizontal line respectively. It is clear therefore that a Carnot cycle forms a rectangle on a T-S diagram regardless of the nature of working substance.

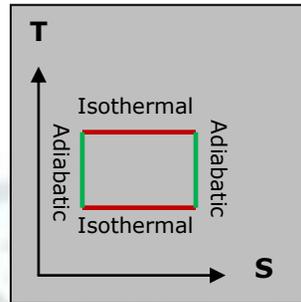


Figure 8.5: T-S diagram representing a Carnot cycle.

Interesting facts

- ✓ To work with T-S diagrams in the analysis of Carnot engines and their efficiency is found convenient as one can find out the efficiency of the same directly from the T-S diagram. The area under curve on the T-S diagram directly gives the work (W) extracted from heat transferred. The heat absorbed (Q_1) can also be calculated easily using relation $dQ = T dS$. Therefore, efficiency ($\eta = \frac{W}{Q_1}$) of Carnot engines can be easily determined.
- ✓ Only reversible processes can be plotted on T-S diagram because of the definition of entropy.

8.5.2 Slopes of different processes on T-S diagram

Isothermal process: The shape of the curve on a T-S diagram is determined by the nature of the reversible process e.g. a horizontal line on a T-S diagram represents an isothermal process.

Adiabatic process: For an adiabatic process; $dQ = 0$

And, hence from the definition of entropy ($dS = \frac{dQ}{T}$), the change in entropy will be zero. Therefore, an adiabatic process is represented by a vertical line on T-S diagram and the vertical line is called as isentrope.

Isochoric process: Consider a mole of gas is heated at constant volume so that the change in its temperature is dT . Then, we may write

$$dQ = C_v dT \quad (8.8)$$

But from the definition of entropy,

$$dQ = T dS \quad (8.9)$$

So, from equations 8.8 and 8.9,

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$$TdS = CvdT$$

Or

$$\left(\frac{dT}{dS}\right) \text{ at constant volume} = \frac{T}{Cv} \quad (8.10)$$

Isobaric process: Similarly, for isobaric process, we can show

$$\left(\frac{dT}{dS}\right) \text{ at constant pressure} = \frac{T}{Cp} \quad (8.11)$$

Now, from equations (8.10) and (8.11),

$$\left(\frac{dT}{dS}\right) \text{ at constant volume} > \left(\frac{dT}{dS}\right) \text{ at constant pressure}$$

And

$$\frac{\left(\frac{dT}{dS}\right) \text{ at constant volume}}{\left(\frac{dT}{dS}\right) \text{ at constant pressure}} = \frac{Cp}{Cv} = \gamma \quad (8.12)$$

Example: A thermodynamic cyclic process is performed via two different cycles as shown in the figure 8.6. Compare the efficiencies of the cycles ABCA.

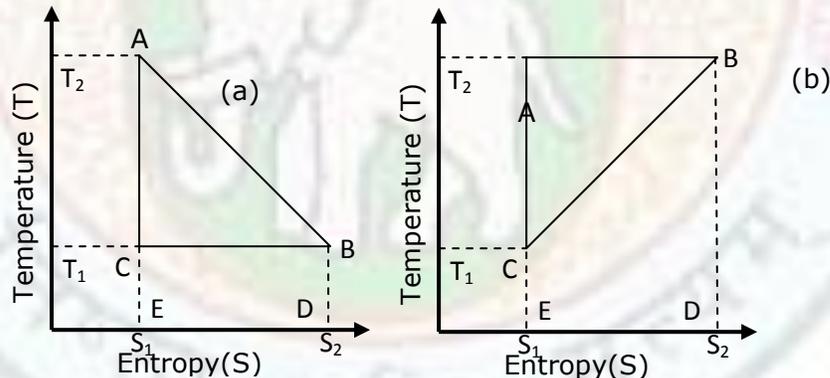


Figure 8.6: T-S diagrams of two different cycles. Here the arms of the triangles are same.

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Solution: From Figure 8.6 (a), the heat supplied to the system (Q_1) will be equal to the area under curve ABDEA *i.e.*

$$Q_1 = T_1 (S_2 - S_1) + \frac{1}{2} (T_2 - T_1)(S_2 - S_1)$$

And the work (W) extracted from this heat will be equal to the area of triangle ABC *i.e.*

$$W = \frac{1}{2} (T_2 - T_1)(S_2 - S_1)$$

From the definition, the efficiency of the cycle ABCA for process (a) is given by

$$\eta_a = \frac{w}{Q_1} = \frac{\frac{1}{2} (T_2 - T_1)(S_2 - S_1)}{T_1 (S_2 - S_1) + \frac{1}{2} (T_2 - T_1)(S_2 - S_1)} \dots \dots \dots (8.13)$$

Now, for the cycle shown in figure 8.6 (b), the heat supplied, Q_1 and work obtained, W will readily be as follows;

$$Q_1 = T_2(S_2 - S_1),$$

$$W = \frac{1}{2} (T_2 - T_1)(S_2 - S_1)$$

So, the efficiency of the cycle ABCA for process (b) will be

$$\eta_b = \frac{w}{Q_1} = \frac{\frac{1}{2} (T_2 - T_1)(S_2 - S_1)}{T_2 (S_2 - S_1)} \dots \dots \dots (8.14)$$

From equations 8.13 and 8.14,

$$\frac{\eta_a}{\eta_b} = \frac{2T_2}{T_1 + T_2}$$

8.6 Summary

Clausius theorem: The integral of the ratio of heat transferred and temperature (at which the heat is transferred) in a reversible thermodynamic process is always comes out to be zero. Mathematically

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

Where, \oint stands for the integration taken for complete cycle.

Entropy: Mathematically, entropy is a thermodynamic state function whose value at final state minus its value at initial state is equal to the integral $\int_R \frac{dQ}{T}$. If a small amount of heat dQ is transferred to any system at constant temperature T , then the change in entropy is given by

$$dS = \frac{dQ}{T}$$

Clausius inequality: The ratio of heat transferred and temperature *at which heat is transferred* in an internal irreversible thermodynamic cycle is always less than zero i.e.

$$\oint \frac{dQ}{T} < 0, \text{ (for irreversible cycle)}$$

T-S diagram: A diagram in which temperature T is plotted (on X-axis) against entropy S (on Y-axis) is called as T-S diagram.

8.7 Exercise

8.7.1 Subjective questions

1. State and establish Clausius theorem.
2. Define entropy and write down its physical significance.
3. Show that change in entropy is path independent for a reversible process.
4. Express second law of thermodynamics in terms of entropy.
5. State and deduce Clausius inequality.
6. Sketch T-S diagram for a Carnot cycle and derive the expression for the efficiency of Carnot engine directly from it.
7. Find out the expressions for the slope of an isochoric and isobaric processes on T-S diagram.
8. Show that the slope of an isochoric curve on T-S diagram is greater than that of isobaric one at the same temperature.
9. Prove that

$$\oint Tds = \oint PdV$$

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8.7.2 Objective questions

1. True or false

- a) Second law of thermodynamics expresses the concept of temperature.
- b) Internal energy of a system is a state function.
- c) Second law of thermodynamics expresses the concept of entropy.
- d) Entropy is a path dependent function.

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|----------------------------------|--|
| Correct answer/option (s) | (a) False (b) True (c) True (d) False |
|----------------------------------|--|

Justification/feedback for correct answer (s)

- a) The concept of temperature is expressible from zeroth law of thermodynamics.
- b) The internal energy of a system depends only on state (final and initial) points, not on the path.
- c) The concept of entropy is contained in the second law of thermodynamics.
- d) Entropy is a state function change in which is path independent.

2. True or false

- a) Heat of any thermodynamic system is a point function.
- b) Internal energy is an inexact differential.
- c) Entropy remains constant in an adiabatic change.
- d) In an isothermal process, internal energy does not change.

| | |
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| Correct answer/option (s) | (a) False (b) False (c) True (d) True |
|----------------------------------|--|

Justification/feedback for correct answer (s)

- a) Heat is a path dependent function.
- b) Internal energy of a system depends only on state (final and initial) points, not on the path and hence is an exact differential.
- c) From the definition of entropy, $dS = dQ/T$; $dS = 0$, for $dQ = 0$.
- d) The internal energy is a function of temperature and for isothermal process $dT = 0$.

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3. True or false

- a) For a complete reversible cycle, entropy remains constant.
- b) The integral $\oint \frac{dQ}{T}$ is always zero for an irreversible cycle.
- c) The integral $\oint \frac{dQ}{T}$ is less than zero a reversible cycle.
- d) All natural processes are isentropic.

| | |
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| Correct answer/option (s) | (a) True (b) False (c) False (d) False |
|----------------------------------|---|

Justification/feedback for correct answer (s)

- a) From Clausius theorem ($\oint_R \frac{dQ}{T} = 0$), clearly, entropy remains constant for a complete reversible cycle.
- b) From Clausius inequality, the integral $\oint \frac{dQ}{T}$ comes out to be less than zero for an irreversible process.
- c) Same as b)
- d) Natural processes are irreversible and hence are not isentropic.

4. True or false

- a) Entropy does not change in a Carnot cycle.
- b) Entropy remains constant during the melting of ice at constant temperature.
- c) In the process of sublimation, entropy increases.
- d) During the freezing of water into ice, entropy increases.

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| Correct answer/option (s) | (a) True (b) False (c) True (d) False |
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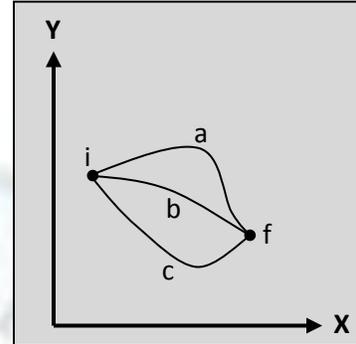
Justification/feedback for correct answer (s)

- a) During the complete Carnot cycle, the system restores its original state and hence entropy remains constant.
- b) In the process of melting, the constituent molecules of water changes from a highly ordered state to a disordered state and hence entropy increases.
- c) In the process of sublimation, the constituent molecules changes from a highly ordered state to a disordered state and hence entropy increases.
- d) Freezing is opposite process to melting and hence entropy decreases.

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8.7.3 Multiple choice questions

1. A thermodynamic system is taken from an initial state i to a final state f in three different paths as shown in figure. Choose the correct option



- (a) The entropy change is maximum in process a
- (b) The entropy change is maximum in process b
- (c) The entropy change is maximum in process c
- (d) The entropy change is the same all three processes

2. According to the Clausius theorem

- (a) $\oint_R \frac{dQ}{T} = \text{constant}$
- (b) $\oint_R \frac{dQ}{T} \leq 0$
- (c) $\oint_R \frac{dQ}{T} > 0$
- (d) $\oint_R \frac{dQ}{T} = 0$

3. On a T-S diagram, the area under curve represents

- (a) Heat absorbed
- (b) Heat converted into work
- (c) Efficiency of Carnot cycle
- (d) Both (a) and (b)

4. For a complete thermodynamic cyclic process,

- (a) $PdV = TdS$
- (b) $dU + PdV = TdS$
- (c) $PdV < TdS$
- (d) $dU = TdS$

5. On a T-S diagram, a horizontal line represents

- (a) Isobaric process
- (b) Isothermal process
- (c) Adiabatic process
- (d) Isochric process

6. The adiabatic curve on a T-S diagram is

- (a) A horizontal line
- (b) A vertical line
- (c) Line making 45° angle with T-axis
- (d) None of these

8.8 Glossary

State functions: The thermodynamic functions whose values depend only on the thermodynamic co-ordinates of the final and initial states, not on the path by which the system is taken from initial to final state e.g. internal energy.

Generalized work diagram: A generalized force such as Pressure, surface tension, electromotive force, magnetic induction when plotted against their corresponding generalized displacement such as volume, area, potential and magnetization respectively, constitute a generalized work diagram.

C_p : It is the heat capacity of the material (such as gas) at constant pressure. C_p of a substance is defined as "the minimum amount of heat (in calories) required for increasing the temperature of one gram of that substance by 1°C at constant pressure".

C_v : It is the heat capacity of the material (such as gas) at constant volume. C_v of a substance is defined as "the minimum amount of heat (in calories) required for increasing the temperature of one gram of that substance by 1°C at constant pressure".

γ : It is the ratio of C_p and C_v

8.9 References

Book cited:

Heat and Thermodynamics: An Intermediate Text Book by Mark W. Zemansky and Richard H. Dittman (McGra-Hill, 1993).

The Physical World of Chemistry, by Keith J. Laidler, (Oxford University Press, 1995). (for historical part).

Further readings

1. Thermodynamics by Enrico Fermi (Courier Dover Publications, 1956)
2. Thermal Physics by Garg, Bansal and Ghosh (Tata McGra-Hill, 1993)
3. A Treatise on Heat: Including Kinetic Theory of Gases, Thermodynamics and Recent advances in Statistical Thermodynamics by Meghnad Saha, B.N. Srivastava (Indian Press, 1958)