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PHYSICS DEPARTMENT

E-Content

On

Basic Concept of the Entropy

(Part-III)

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The Entropy, principle of increase of entropy and its calculations

Basic Objectives: The Students will be introduced basic concepts and definitions of entropy, physical significance, principle of increase of entropy and calculations.

Entropy

If talk about the first law of thermodynamic, we initially stated the law in terms of a cycle, but we then defined a property, the internal energy, that enabled us to use the first law quantitatively for processes. Similarly, we have stated the second law of thermodynamics for a cycle, and we now find that the second law leads to a property, entropy, that enables us to treat the second law quantitatively for processes. Energy and entropy are both abstract concepts that help to describe certain observations.

1. Entropy:

In 1854, The Claussius introduced the concept of entropy while they are studying the second law of thermodynamics and its applications. It is a very important thermodynamic quantity and used to the study of heat engine. *The entropy is the physical quantity of the substance, which remains unchanged during the reversible adiabatic process.*

If any substance at a constant temperature T , heat energy δQ has been either absorbed or librated in any reversible process then the ratio of $\delta Q/T$, is called the increase or decrease of entropy of that substance. Therefore

$$\delta S = \frac{\delta Q}{T} \text{----- (1)}$$

For infinitesimal change, it is denoted as

$$dS = \frac{dQ}{T} \text{----- (2)}$$

Unit of the entropy: *Joule/ deg. Kelvin or Erg/ deg. Kelvin or calorie / deg. Kelvin.*

1.1 Physical Significance:

$$dS = \frac{dQ}{T}$$
$$dQ = TdS \text{----- (3)}$$

It is clear from the above relation that heat energy has the same dimension as the product of entropy and absolute temperature. Since the gravitational potential energy of a body is proportional to the product of its mass and height above some zero level hence if we may take temperature equivalent to height we may regard entropy as analogous to mass. Therefore, entropy may be thought as thermal inertia which has the same relation with heat motion as mass bears to linear motion or moment of inertia bears to rotational motion.

3. Calculation of the entropy in various cases:

3.1. Entropy change in adiabatic process:

In the adiabatic process, the heat is not absorbed nor librated i.e. $dQ = 0$. Therefore the entropy change in adiabatic process

$$dS = \frac{dQ}{T} = 0 \Rightarrow dS = 0 \text{ i.e. } S = \text{Constant}$$

It is clear that entropy change in adiabatic process is zero. In the other words, entropy of the system remains constant in adiabatic process. The adiabatic curves are called isoentropics.

3.2 Entropy change in isothermal process:

Let us consider the temperature (T), the Volume (V) and Pressure (P) of one gram mole of perfect gas. If the isothermal change is being on in the gas, then from the First Law of Thermodynamics,

$$dQ = dU + dW$$

But for isothermal process $dU = 0$

Therefore $dQ = dW = PdV \quad \therefore PV = RT = \text{constant}$

Hence, the entropy changes in isothermal process;

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

On integrating on both sides, we have

$$\int_{S_1}^{S_2} dS = \int_{V_1}^{V_2} \frac{PdV}{T}$$

$$S_2 - S_1 = R \int_{V_1}^{V_2} \frac{dV}{V} \quad \therefore P/T = R/V$$

$$S_2 - S_1 = R \log_e \left(\frac{V_2}{V_1} \right) = 2.3026 R \log_{10} \left(\frac{V_2}{V_1} \right) \quad \text{----- (4)}$$

3.3 Entropy change in reversible process:

Let us consider a reversible cycle (Carnot's engine) ABCD has shown in Fig. 1.

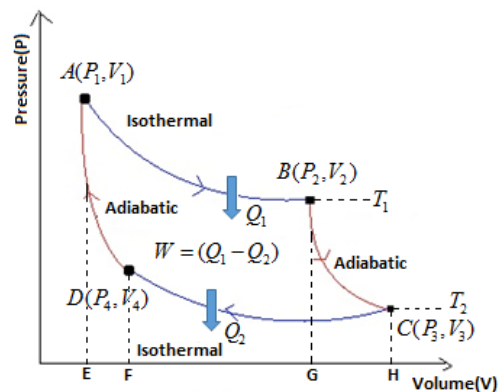


Fig. 1

In isothermal process AB, the working substance absorbs an amount of heat Q_1 at a constant temperature T_1 of the source. By this, the decrease in entropy of the source $= \frac{Q_1}{T_1}$

The BC is adiabatic process, thus entropy change in BC adiabatic process $= 0$

In the process CD (isothermal process), the working substance rejects the heat Q_2 at a constant temperature T_2 to the sink. Thus, increase in the entropy in the process CD $= \frac{Q_2}{T_2}$

The DA process is adiabatic process. Thus entropy change in DA process $= \text{zero}$.

Thus, the increase in entropy in the complete cycle,

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} + 0 + 0 = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \text{----- (5)}$$

From Definition of Carnot's engine,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \text{----- (6)}$$

Hence, from eq. (5) and eq. (6),

$$\Delta S = 0 \Rightarrow S = \text{Constant}$$

Thus, in a cycle of reversible process, the entropy of the system remains constant or the change in entropy of the system is zero.

3.4 Entropy Change in an irreversible process:

Let us suppose that a reversible engine has the efficiency η and takes in a quantity of heat Q_1 at the temperature T_1 from the source and rejects the heat Q_2 at the temperature T_2 to the sink, then

$$\eta = 1 - \frac{T_2}{T_1}$$

If engine is irreversible and its efficiency be η' , then

$$\eta = 1 - \frac{Q_2}{Q_1}$$

Since,

$$\begin{aligned} \eta &> \eta' \\ \Rightarrow 1 - \frac{T_2}{T_1} &> 1 - \frac{Q_2}{Q_1} \\ \Rightarrow -\frac{T_2}{T_1} &> -\frac{Q_2}{Q_1} \\ \Rightarrow \frac{T_2}{T_1} &< \frac{Q_2}{Q_1} \\ \Rightarrow \frac{Q_2}{T_2} &> \frac{Q_1}{T_1} \end{aligned}$$

$$\Rightarrow \frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0$$

$$\Rightarrow \Delta S > 0$$

Thus, the entropy increases in the irreversible process. This is also called the **Clausius Theorem**.

3.5 The Expression for the Entropy Change for the Solid or Liquid of change the temperatures from T_1 °K to T_2 °K :

Let us assume that a solid or gas of m gram mass having the specific heat s , be heated from T_1 °K to T_2 °K. if dQ heat given to the solid or liquid, increase in temperature be the dT , then

$$dQ = msdT$$

Then entropy change is given as,

$$\Delta S = \int \frac{dQ}{T} = \int_{T_1}^{T_2} ms \frac{dT}{T}$$

$$\Delta S = ms \log_e \left(\frac{T_2}{T_1} \right) \quad \text{----- (6)}$$

$$\Delta S = 2.3026 ms \log_{10} \left(\frac{T_2}{T_1} \right) \quad \text{----- (7)}$$

If $T_2 > T_1$, so the value of $\Delta S = dS = +ve$, therefore the increase in the temperature, the entropy also increases.

3.6 Determination of the Entropy change when the substances change the state at the constant temperature:

Let m gram substance change the state at constant temperature T , the value of dQ in the change of state thus $dQ = mL$, where L is the latent heat.

$$\text{Thus the change in entropy } dS = \frac{dQ}{T} = \frac{mL}{T} \quad \text{----- (8)}$$

3.7 Entropy change in Vander waal's gas:

We know the intermolecular attraction in Vander waal's gas be the $\frac{a}{V^2}$, thus work done against the intermolecular attraction, the from the first law of thermodynamics,

$$dQ = dU + dW$$

$$dQ = dU + P'dV$$

$$dQ = dU + \left(P + \frac{a}{V^2} \right) dV$$

$$dQ = C_V dT + \left(P + \frac{a}{V^2} \right) dV \quad \text{----- (9)}$$

Entropy change for the state change from the State A to the State B,

$$\int_{S_A}^{S_B} dS = \int_A^B \frac{dQ}{T} = \int_A^B \frac{(C_V dT + (P + \frac{a}{V^2}) dV)}{T}$$

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{(P + \frac{a}{V^2})dV}{T} \quad \text{----- (10)}$$

Vander Waal's gas equation for one gram mole

$$\begin{aligned} \left(P + \frac{a}{V^2}\right)(V - b) &= RT \\ \Rightarrow \left(P + \frac{a}{V^2}\right) &= \frac{RT}{V-b} \end{aligned} \quad \text{----- (11)}$$

From the eq. (10) and eq. (11), we have

$$\begin{aligned} S_B - S_A &= C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{RTdV}{T(V-b)} \\ S_B - S_A &= C_V \log_e \left(\frac{T_B}{T_A}\right) + R \log_e \left(\frac{V_B-b}{V_A-b}\right) \end{aligned} \quad \text{----- (12)}$$

$$S_B - S_A = 2.3026 \left[C_V \log_e \left(\frac{T_B}{T_A}\right) + R \log_e \left(\frac{V_B-b}{V_A-b}\right) \right] \quad \text{----- (13)}$$

This is the required expression for the change in entropy for the Vander Waal's gas.

3.8 Determination of the Entropy change when the ice converts to the steam:

Let the ice at temperature T_1 ⁰K has been melted and convert in the water, then the entropy change

$$dS_1 = \frac{mL_1}{T_1} \quad \text{----- (14)}$$

Where L_1 = The latent heat of the ice.

When the temperature of the water has change from the T_1 ⁰K to T_2 ⁰K, then the entropy change

$$dS_2 = ms \log_e \left(\frac{T_2}{T_1}\right) = 2.3026 ms \log_{10} \left(\frac{T_2}{T_1}\right) \quad \text{----- (15)}$$

When the water at temperature T_2 ⁰K is converted in to the steam at the same temperature, it absorbs the L_2 heat, where L_2 is the latent heat of steam. Therefore the entropy change

$$dS_3 = \frac{mL_2}{T_2} \quad \text{----- (16)}$$

Thus, the total entropy change, when the ice converts into steam, then

$$\begin{aligned} dS &= dS_1 + dS_2 + dS_3 \\ dS &= \frac{mL_1}{T_1} + 2.3026 ms \log_{10} \left(\frac{T_2}{T_1}\right) + \frac{mL_2}{T_2} \end{aligned} \quad \text{----- (17)}$$

This is the expression for the steam change from the ice.

3.9 The entropy change of a perfect gas:

Case-I: Let us consider the pressure P_1 , volume V_1 and the temperature T_1 is for one gram the perfect gas, then the entropy change

$$dS = \frac{dQ}{T} \quad \text{----- (18)}$$

From the first law of thermodynamics,

$$dQ = dU + dW$$

$$dQ = C_V dT + PdV$$

Therefore,
$$dS = \frac{C_V dT + PdV}{T} \quad \text{----- (19)}$$

Case-a: In terms of T & V: If the gas has been changing the state A (P_A, T_A, V_A) to state B (P_B, T_B, V_B), then the entropy change

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{PdV}{T}$$

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{RdV}{V} \quad \therefore P/T = R/V$$

$$S_B - S_A = C_V \log_e \left(\frac{T_B}{T_A} \right) + R \log_e \left(\frac{V_B}{V_A} \right) \quad \text{----- (20)}$$

$$S_B - S_A = 2.3026 \left[C_V \log_e \left(\frac{T_B}{T_A} \right) + R \log_e \left(\frac{V_B}{V_A} \right) \right] \quad \text{----- (21)}$$

The entropy change for any state

$$S = S_0 + C_V \log_e T + R \log_e V \quad \text{----- (22)}$$

Case-b: In terms of T & P:

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{PdV}{T}$$

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{PdV}{T} \quad \text{----- (23)}$$

$$\therefore PV = RT \Rightarrow PdV + VdP = RdT \Rightarrow PdV = RdT - VdP \quad \text{----- (24)}$$

But from Mayer's formula,

$$C_P - C_V = R \quad \text{----- (25)}$$

Using the eq. (24) and (25), then eq. (23) becomes as

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_A^B \frac{RdT - VdP}{T}$$

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + (C_P - C_V) \int_{T_A}^{T_B} \frac{dT}{T} - \int_{V_A}^{V_B} \frac{RdP}{P} \quad \therefore V/T = R/P$$

$$S_B - S_A = C_P \log_e \left(\frac{T_B}{T_A} \right) - R \log_e \left(\frac{P_B}{P_A} \right) \quad \text{----- (26)}$$

$$S_B - S_A = 2.3026 \left[C_P \log_{10} \left(\frac{T_B}{T_A} \right) - R \log_{10} \left(\frac{P_B}{P_A} \right) \right] \quad \text{----- (27)}$$

The entropy change of the perfect gas equation in any state

$$S = S_0 + C_P \log_e T + R \log_e P \quad \text{----- (28)}$$

Case-C: In terms of P & V:

From eq. (2), we have

$$S_B - S_A = C_V \int_{T_A}^{T_B} \frac{dT}{T} + \int_{V_A}^{V_B} \frac{PdV}{T} \quad \text{----- (29)}$$

$$\therefore PV = RT \Rightarrow PdV + VdP = RdT \Rightarrow dT = \frac{PdV + VdP}{R}$$

$$S_B - S_A = C_V \int_A^B \frac{PdV + VdP}{PV} + \int_{V_A}^{V_B} \frac{RdV}{V} \quad \therefore PV = RT \Rightarrow \frac{P}{T} = \frac{R}{V}$$

$$S_B - S_A = C_V \int_{P_A}^{P_B} \frac{dP}{P} + C_V \int_{V_A}^{V_B} \frac{dV}{V} + (C_P - C_V) \int_{V_A}^{V_B} \frac{dV}{V}$$

$$S_B - S_A = C_V \int_{P_A}^{P_B} \frac{dP}{P} + C_P \int_{V_A}^{V_B} \frac{dV}{V}$$

$$S_B - S_A = C_V \log_e \left(\frac{P_B}{P_A} \right) + C_P \log_e \left(\frac{V_B}{V_A} \right) \quad \text{----- (30)}$$

$$S_B - S_A = 2.3026 \left[C_V \log_{10} \left(\frac{P_B}{P_A} \right) + C_P \log_{10} \left(\frac{V_B}{V_A} \right) \right] \quad \text{----- (31)}$$

The entropy change of the perfect gas equation in any state

$$S = S_0 + C_V \log_e P + C_P \log_e V \quad \text{----- (32)}$$

(1) If pressure is constant then entropy change ($P_A = P_B$)

$$S_B - S_A = 2.3026 \left[\log_{10} \left(\frac{V_B}{V_A} \right) \right]$$

(2) If volume is constant then entropy change ($V_A = V_B$)

$$S_B - S_A = 2.3026 \left[C_V \log_{10} \left(\frac{T_B}{T_A} \right) \right]$$

(3) If temperature is constant then entropy change ($T_A = T_B$)

$$S_B - S_A = -2.3026 \left[R \log_{10} \left(\frac{P_B}{P_A} \right) \right]$$

4. Second Law of Thermodynamics in terms of Entropy:

From the first law of thermodynamics,

$$dQ = dU + dW \quad \text{----- (33)}$$

From the Second law of thermodynamics,

$$dQ = TdS \quad \text{----- (34)}$$

Therefore, from eq. (33) and eq. (34), we have

$$TdS = dU + dW \quad \text{----- (35)}$$

This is the *fundamental relation of thermodynamics*.

5. Principle of Increase of Entropy:

“There is an increase in entropy of the system during an irreversible process and entropy remains constant in reversible process.”

Analytically, we can write this statement given as follow:

$$\Delta S \geq 0$$

This statement is called *Principle of Increase of Entropy*.

Proof: Let A and B are two bodies having the temperatures T_1 ⁰K and T_2 ⁰K ($T_1 > T_2$) respectively.

The amount of the heat dQ transfer from A to B, decrease in entropy of Body A = $\frac{dQ}{T_1}$

Increase in entropy of Body B = $\frac{dQ}{T_2}$

Therefore, the net increase in the entropy of the system = $\frac{dQ}{T_2} - \frac{dQ}{T_1} = dQ \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
 $= dQ \left(\frac{T_1 - T_2}{T_1 T_2} \right) = +ve$

Thus, *the entropy of an isolated or self-contained system either increases or remains constant according to irreversible or reversible process.*

Temperature-Entropy Diagram (T-S Diagram):

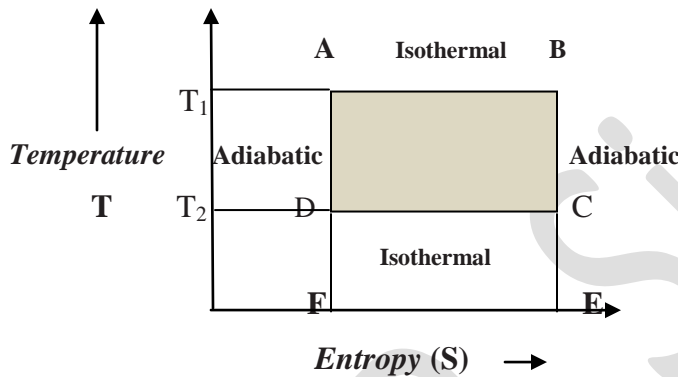


Fig. 1: T-S Diagram

The work of the heat engine can be represented by the plot between the change in entropy of the working substance and absolute temperature. The graph between the entropy (S) and temperature (T) represent the thermodynamics state of any system and called the T-S diagram. The Carnot's reversible cycle has been shown on the T-S diagram in fig.1. AB and CD are two isotherms having temperatures T_1 °K and T_2 °K ($T_1 > T_2$) as on ordinate and parallel to the axis of entropy. Two adiabatic BC and DA are parallel to temperature axis on abscissa.

In the isothermal process AB, the heat Q_1 taken from the source = $Area ABCD = T_1(S_2 - S_1)$

In the isothermal compression CD, the heat Q_2 given to the sink = $Area CEFD = T_2(S_2 - S_1)$

The heat change in the work = $W = Q_1 - Q_2 = T_1(S_2 - S_1) - T_2(S_2 - S_1)$
 $= (S_2 - S_1)(T_1 - T_2)$

Thus, the efficiency of Carnot's engine $\eta = \frac{W}{Q_1} = \frac{(S_2 - S_1)(T_1 - T_2)}{T_1(S_2 - S_1)}$

$$\therefore \eta = 1 - \frac{T_2}{T_1}$$

Which is the relation of the efficiency of Carnot's engine. Thus, *the importance of the TS-diagram used to test the efficiency of the actual engine.*

Q.1: Prove that

$$\oint TdS = \oint PdV$$

Solution: From the first law of thermodynamics,

$$dQ = dU + dW \quad \text{----- (a)}$$

From the Second law of thermodynamics,

$$dQ = TdS \quad \text{----- (b)}$$

Therefore, from eq. (a) and eq. (b), we have

$$TdS = dU + dW \quad \text{----- (c)}$$

On integrating eq. (c) for a closed path (cyclic process), Thus

$$\oint TdS = \oint dU + \oint dW$$

$$\oint TdS = \oint dU + \oint PdV \quad \therefore dW = PdV$$

For the cyclic process, $\oint dU = 0$ (because of the internal energy becomes zero in the cyclic process), therefore

$$\oint TdS = \oint PdV$$