

UNIT - II

THERMODYNAMICS - II

Second Law of Thermodynamics

NEED FOR THE LAW (Limitations of the first law)

1. The first law gives a definite relationship between the heat absorbed Q , and the work done W , by a system in a given process. *But it does not give the direction of the flow of heat.*

E.g., We know from experience that transfer of heat from a lower temperature to a higher temperature is not possible without spending energy. i.e., spontaneously. But according to first law both transfers are possible which is not correct. This means that first law is unable to give the direction of the flow of heat.

2. According to first law the energy of an isolated system remains constant during a particular change of state. *But it is unable to predict the feasibility of a reaction i.e. it is unable to tell whether a change of state or a reaction can take place spontaneously (on its own accord) or not.*

E.g., We know by experience that a metal rod of uniform temperature cannot become cooler at one end hotter at the other **on its own accord**. i.e., This process is NOT FEASIBLE. But according to first law this process is not impossible. It only stipulates the conditions that this process takes place, then the heat lost at one end will be equal to heat gained at the other.

3. According to first law one form of energy can be converted into another. But it does not indicate the fact that heat energy can not be converted **completely** into work.

Because of the limitations of the first law we need another law to predict direction of flow of heat, to predict the feasibility of a reaction and to find out the fraction of heat absorbed that could be converted into work. That is why we need II law of thermodynamics which gives answer to all the above mentioned points.

From second law, we define a new thermodynamic property called

from a point at a higher potential to a point at a lower potential on its own accord. But the reverse does not happen on its own accord.

5. Entropy of the universe which is a measure of unavailable energy and randomness, is increasing.
6. Free energy of the universe which is a measure of available energy for work is decreasing.

Heat Engine

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of a suitable device.

A machine which can do work by using heat that flows out spontaneously from a high temperature source to a low temperature sink is called heat engine. A steam engine is a typical heat engine. It takes heat from the boiler (high temperature source) converts some heat to work and returns the unused heat to the surroundings (low temperature sink).

CARNOT CYCLE AND ITS EFFICIENCY

Carnot's Cycle

Some definitions :

- i) **Carnots engine:** The hypothetical heat engine designed by Carnot is known as Carnot engine. In a Carnot engine the working substance is one mole of an ideal gas. The engine is capable of working reversibly between two temperature T_2 and T_1 where $T_2 > T_1$.
- ii) **Cycle process :** When a system, after completing a series of changes returns to its original state, it is said to have completed a cycle. Such a process is known as a cyclic process. We know that internal energy E - depends only upon the state of a system.

In a cyclic process, as the system returns back to its original state,

$$\Delta E = 0; \quad \text{i.e., } \Delta E = Q - W = 0$$

$$Q - W = 0; \quad \text{i.e., } Q = W$$

3. Carnot cycle : A single cycle of the Carnot's engine is referred to as Carnot cycle. For a single cycle of Carnot engine, the ideal gas undergoes the following changes.

1. Reversible isothermal expansion.
2. Reversible adiabatic expansion.
3. Reversible isothermal compression and
4. Reversible adiabatic compression.

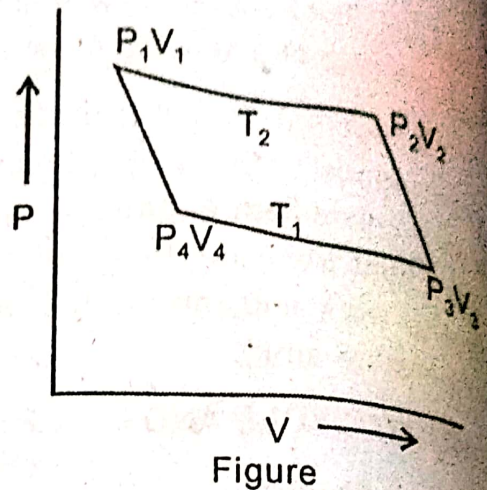
Carnot's cycle is used to show the maximum convertibility of heat into work.

4. Efficiency of heat engine (η)

$$\eta = \frac{\text{Work done}}{\text{Heat absorbed}} = \frac{W}{Q}$$

Derivation of an expression for the efficiency of Carnot's engine:

Carnot's reversible cycle: The pressure and volume of the ideal gas change during the Carnot cycle as shown by Figure.



1. Reversible isothermal expansion:

One mole of the ideal gas absorbs heat from the reservoir at T_2 and expands isothermally and reversibly. The volume of the gas changes from V_1 to V_2 . During this change;

$$\text{Heat change} = Q_2; \quad \text{Work done} = W_1$$

$$W_1 = RT_2 \ln \frac{V_2}{V_1}$$

Since the gas is ideal $Q_2 = W_1$;

2. Reversible adiabatic expansion :

In the second stage, the ideal gas at T_2 is allowed to expand adiabatically. The volume changes from V_2 to V_3 and temperature reduces to T_1 .

$$\text{heat change} = 0$$

$$\text{Work done } W_2 = C_v \int_{T_2}^{T_1} dT = -C_v (T_1 - T_2)$$

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

3. Reversible isothermal compression:

In the third stage. The gas is placed in the reservoir at T_1 and is compressed isothermally and reversibly such that it gives heat Q_1 to the reservoir. There by the volume decreases from V_3 to V_4 .

$$\text{heat change} = -Q_1$$

$$\text{Work done, } W_3 = RT_1 \ln \frac{V_4}{V_3} \quad W_3 = -Q_1$$

4. Reversible adiabatic compression :

In the fourth stage the gas is compressed adiabatically and the temperature increases from T_1 to T_2 . The volume reduces from V_4 to V_1 . Thus one cycle is completed and the gas returns to the Initial state. During the fourth stage.

$$\text{heat change} = 0$$

$$\text{Work done, } W_4 = -C_v(T_2 - T_1)$$

The total work done in the cycle is the sum of works done in the four stages.

$$W = W_1 + W_2 + W_3 + W_4$$

$$W = RT_2 \ln \frac{V_2}{V_1} - C_v(T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} - C_v(T_2 - T_1)$$

$$W = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

The heat absorbed from the reservoir at T_2

$$Q_2 = RT_2 \ln \frac{V_2}{V_1}$$

$$\text{Efficiency of the engine} = \frac{W}{Q_2}$$

$$\frac{W}{Q_2} = \frac{RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}}{RT_2 \ln \frac{V_2}{V_1}}$$

When we consider the adiabatic expansion in the cycle,

$$T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2} \right)^{\gamma-1}$$

Considering the adiabatic compression,

$$T_1 V_4^{\gamma-1} = T_2 V_1^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_4}{V_1} \right)^{\gamma-1}$$

Comparing (2) and (3)

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}; \quad \text{i.e.} \quad \frac{V_4}{V_3} = \frac{V_1}{V_2}$$

Substituting these in equation (1)

$$\frac{W}{Q_2} = \frac{RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_1}{V_2}}{RT_2 \ln \frac{V_2}{V_1}}$$

$$\frac{W}{Q_2} = \frac{(T_2 - T_1)}{T_2} \times \frac{R \ln \frac{V_2}{V_1}}{R \ln \frac{V_2}{V_1}}$$

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

Thus the efficiency of the Carnot engine is given by the working temperature. Any other heat engine working reversibly between these temperatures will have the same efficiency.

These efficiency does not depend upon the working substances design of the engine etc., because as per the above equation efficiency depends on only the temperature of source and sink and nothing else.

Efficiency of a heat engine is always less than one

We know that

$$\text{Proof: } \eta = \frac{T_2 - T_1}{T_2} = \frac{T_2}{T_2} - \frac{T_1}{T_2}$$

i.e., $\eta < 1$

$$\text{Reason: We know that } \eta = \frac{T_2 - T_1}{T_2}$$

If $T_1 = 0$ then

$$\eta = \frac{T_2 - 0}{T_2} = \frac{T_2}{T_2} = 1$$

i.e., If we use a sink in the carnot cycle, whose temperature is absolute zero (i.e., 0 K) then efficiency will be 1. But 0 K is unattainable. So η will always be less than 1.

A heat engine cannot work between two reservoirs with same temperature. Reason: If $T_2 = T_1$ then efficiency is zero. That means the machine can not work.

REFRIGERATION CYCLE

In the carnot cycle all the steps are reversible. That is the carnot cycle can be operated in the opposite direction where the signs of all the heat and work quantities are reversed. This reverse engine is a **refrigeration cycle**. This reverse engine absorbs heat from the lower temperature, some work is done on it by the surroundings and rejects heat at the higher temperature. It thus functions as a refrigerator, that is, it extracts heat from a cold reservoir and passes it to a hot reservoir. The ratio of work done on the engine to the heat absorbed at lower

entropy. Also we define some other related properties. Studying the changes of these properties in a system, we propose certain conditions for irreversible and reversible processes. These conditions are used to predict the feasibility of a chemical reaction.

DIFFERENT STATEMENTS OF THE SECOND LAW

1. It is impossible to construct a machine working in cycles which can convert heat completely into an equivalent amount of work without producing changes elsewhere.
2. It is impossible for a self-acting machine, without the help of some external agency, to transfer heat from one body at a lower temperature to a higher temperature.
3. All other forms of energy can be completely converted into heat; whereas complete conversion of heat into any other form of energy is not possible.
4. All spontaneous processes are irreversible.
5. In a reversible process the entropy change, ΔS , of the system and the surroundings taken together remains constant. In an irreversible process it increases. i.e., $\Delta S > 0$.
6. In a reversible process the free energy change ΔG , of the system and surroundings taken together remains constant. In an irreversible process it decreases i.e., $\Delta G < 0$.

Explanation :

1. A machine working in cycles converts heat into work only partially. The ratio between work done and heat absorbed is always less than 1.

$$\text{Efficiency of an engine} = \frac{W}{Q} < 1.$$

2. Heat cannot be transferred from a body with a lower temperature to another with a higher temperature by a machine by itself without the help of some external agency.
3. Conversion of any form of energy, namely electrical, chemical, etc., into heat is possible. But heat cannot be **completely** converted into any other form of energy.
4. All natural processes are irreversible. E.g., i) Water flows down a hill spontaneously; it can not climb up a hill spontaneously. ii) Heat flows from the hot end of a body to the cold end. But heat cannot flow from the cold end of a body to the hot end. iii) Electricity flows

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so that we can define the zero of the thermodynamic scale as the lower temperature of a reversible cycle with an efficiency of 1 i.e., The zero of the thermodynamic scale is the lower temperature of a reversible cycle which is capable of converting heat completely into work.

Significance :

We have seen, under Carnot's cycle, that only when the lower temperature of a reversible cycle is the absolute zero on the ideal gas scale of temperature, the efficiency will be 1. Therefore it follows that the thermodynamic scale of temperature and the ideal gas scale of temperature are the same.

CONCEPT OF ENTROPY :

Definition of entropy from the efficiency of Carnot's engine:

Based on second law, we define a new thermodynamic property called entropy. We express the efficiency of a heat engine by the following expression.

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

We know $W = Q_2 - Q_1$

Neglecting the signs of heat quantities it may be said that W is equal to the algebraic sum of Q_2 and Q_1 . Therefore,

$$W = Q_2 + Q_1$$

$$\frac{Q_2 + Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad ; \quad 1 + \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

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

This tells that in a reversible cycle sum of (Q/T) terms is equal to zero. This is stated as

$$\oint \frac{q_{rev}}{T} = 0$$

We know that the cyclic integral of an exact differential is zero
So $\frac{q_{rev}}{T}$ is an exact differential $\frac{q_{rev}}{T}$ is denoted as dS

$$\therefore dS = \frac{q_{rev}}{T}$$

S is called the entropy. It is a state property. If S_1 is the entropy of the system in its initial state and S_2 , at the final state

$$S_2 - S_1 = \Delta S = \int_1^2 \frac{q_{rev}}{T}$$

ΔS is entropy change. It does not depend upon the path in which the system undergoes the change. It depends upon the initial and final states only. **Entropy is an extensive property similar to internal energy.**

Definition:

It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

Change of entropy (ΔS) of a system is defined as the integral of all the terms involving heat change (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly.

$$\text{Mathematically } \Delta S = \int_1^2 \frac{q_{rev}}{T}$$

For an engine working irreversibly the efficiency is less than one. Therefore in a reversible cycle, the sum of (q_{rev}/T) terms is less than zero

$$\oint \frac{q_{irr}}{T} < 0$$

Units of entropy :

CGS units Calories per degree i.e., Cal. deg^{-1} .

This is known as entropy unit i.e., eu.

SI units Joules per degree kelvin i.e., JK^{-1}

Properties of Entropy

Relation of the Entropy Changes to Changes in the other properties of the system :

Consider a reversible expansion. According to first law of thermodynamics.

$$q_{rev} = dE + P_{op} dV$$

Since the expansion is reversible

$$P_{op} dV = PdV ; \therefore P_{rev} = dE + PdV$$

Dividing through out by T

$$\frac{q_{rev}}{T} = \frac{dE}{T} + \frac{P}{T} dV$$

According to the definition of entropy, the equation becomes

$$dS = \frac{1}{T} dE + \frac{P}{T} dV$$

This expression incorporates both first law and second law. It is a general expression for all the changes in a system.

Entropy as a state function - Entropy as a function of V and T

Let us consider the general expression for entropy change.

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad (4)$$

If we consider internal energy as a function of temperature and volume,

$$E = f(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

$$dE = C_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

Substituting this value of dE in equation (4)

$$dS = \frac{1}{T} \left[C_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV \right] + \frac{P}{T} dV$$

$$dS = \frac{C_v}{T} dT + \frac{1}{T} \left(\frac{\partial E}{\partial V} \right)_T dV + \frac{P}{T} dV$$

$$dS = \frac{C_v}{T} dT + \left[\frac{1}{T} P + \left(\frac{\partial E}{\partial V} \right)_T \right] dV$$

At constant volume $dV = 0$

$$\therefore dS_v = \frac{C_v}{T} dT : \Delta S_v = \int \frac{C_v}{T} dT$$

This relation gives the entropy change of the system at constant volume.

At constant temperature $dT = 0$

$$dS_T = 0 + \frac{1}{T} \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] dV_T$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right]$$

From this expression we can get the following equation

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\beta}$$

This relates entropy change with volume at constant temperature α is coefficient of expansion and β is coefficient of compressibility.

Entropy as a Function of P and T

Consider the general expression for the change in entropy.

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad (4)$$

Consider also the definition of enthalpy

$$E = H - PV; \quad dE = dH - PdV - VdP$$

Substituting this value of dE in equation (4)

$$dS = \frac{dH}{T} - \frac{V}{T} dP \quad (5)$$

If we consider enthalpy as a function of temperature and pressure

$$dH = C_p dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

Substituting this value of dH in (5)

$$dS = \frac{C_p}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] dP$$

At constant pressure $dP = 0$

$$\therefore dS = \frac{C_p}{T} dT; \quad \Delta S = \int_1^2 \frac{C_p}{T} dT$$

This equation relates entropy change with temperature, at constant pressure.

At constant temperature the above equation(6) reduces to

$$dS = -V \alpha dP; \quad \left(\frac{\partial S}{\partial P} \right)_T = -V \alpha$$

V is molar volume and α is coefficient of expansion.

Temperature Dependence of Entropy : If we keep the pressure and volume as constants, the entropy of the system changes with temperature. At constant volume.

$$dS = \frac{C_v}{T} dT$$

and at constant $dS = \frac{C_p}{T} dT$

$$\text{Therefore } C_v = T \left(\frac{\partial S}{\partial T} \right)_v ; C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

Entropy change in ideal gases

Entropy change in isothermal expansion of an ideal gas

From First law $\Delta E = Q - W$

In an isothermal reversible expansion of an ideal gas $\Delta E = 0$

$$\therefore Q_{rev} - W = 0 ; \text{ i.e., } Q_{rev} = W$$

We know work done in such a case

$$W = nRT \ln \frac{V_2}{V_1} ; \therefore Q_{rev} = nRT \ln \frac{V_2}{V_1}$$

$$\text{Dividing through out by } T \quad \frac{Q_{rev}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\text{But by definition } \frac{Q_{rev}}{T} = \Delta S ; \Delta S = nR \ln \frac{V_2}{V_1}$$

Entropy change when V and T are the variables :

The general expression for the entropy change of any system give below.

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad (4)$$

For an ideal gas $dE = C_v dT$

$$\therefore dS = \frac{C_v}{T} dT + \frac{P}{T} dV$$

For one mole of an ideal gas $P = RT/V$.

Substituting this value of P in the above equation

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

Integrating this equation between limites.

$${}_1 \int_2 dS = \frac{C_v}{T} \int_1^{T_2} dT + R \int_{V_1}^V dV$$

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

Entropy change when P and T are the variables

We know, from definition $E = H - PV$

$$dE = dH - PdV - VdP$$

Substituting this value of dE in equation (4)

$$dS = \frac{1}{T} (dH - PdV - VdP) + \frac{P}{T} dV$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

For an ideal gas $dH = C_p dT$;

$$dS = \frac{1}{T} C_p dT - \frac{V}{T} dP$$

For one mole of an ideal gas $V = RT/P$

$$dS = \frac{1}{T} C_p dT - \frac{R}{P} dP$$

Integrating between limits

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Summary : Entropy changes in isothermal (constant temperature) processes

$$\Delta S_T = R \ln \frac{V_2}{V_1} = 2.303 R \log \frac{V_2}{V_1} \quad (\text{or})$$

$$\Delta S_T = R \ln \frac{P_1}{P_2} = 2.303 R \log \frac{P_1}{P_2}$$

Entropy changes in isobaric (constant pressure) processes

$$\Delta S_p = C_p \ln (T_2/T_1) = 2.303 C_p \log (T_2/T_1)$$

Entropy changes in isochoric (constant volume) processes

$$\Delta S_v = C_v \ln (T_2/T_1) = 2.303 C_v \log (T_2/T_1)$$