UNIT – 3

**Limitations of First Law of Thermodynamics**

If a well insulated tank of fluid is stirred by a rotating paddle wheel, the energy of the fluid increases. If the stirrer is stopped, however the energy of the fluid will not decrease and cause the stirrer to rotate in the opposite direction. The possibility of this process proceeding in the opposite direction is not excluded by the first law of Thermodynamics. *Hence first law of thermodynamics does not allow us to* *predict whether a proposed conceived energy conversion is possible or not.*

  In all the internal combustion engines fuel and air mixture is supplied at room temperature. This mixture undergoes combustion inside the engine and gives out work. Exhaust gases coming out of the engine are always at higher temperature, indicating that some heat is taken away into atmosphere. Hence, in all the IC engines only a part of the heat is converted into work. From our experience we know that if any attempt is made to convert all the heat into work, our effort will go in vain. *This limitation in the* *extent of energy conversion has also not been addressed in first law of thermodynamics.*

The first law of thermodynamics tells us that energy can be changed from  one form to another but can be neither created nor destroyed in any process. The mathematical expression which is used to represent the first law of thermodynamics is DE = q-w, where DE refers to the internal energy change of the system when 'w' amount of work is done by the system when it absorbs 'q' amount of heat and carries out 'w' amount of work. However, this law possesses many limitations such as given below.

1. The first law of thermodynamics merely indicates that in any process there is a transformation between the various forms of energy involved in the process but provides no information regarding the feasibility of such transformation.

2. First law does not provide any information regarding the direction a processes will take whether it is a spontaneous or a non spontaneous process.

**The Second law of Thermodynamics**

 **Kelvin Planck’s**: *It is impossible* **statement** *to constructa device that, operating continuously, will**produce no effect other than transfer of heat from a single thermal reservoir and performance of an equal amount of work.*

  The term thermal reservoir refers to a very large system in stable equilibrium, to which or from which, any amount of heat can be transferred at constant temperature.

  A thermal reservoir supplying heat continuously at constant temperature is known as source. (Example : Sun)

  A thermal resevoir receiving heat continuously at constant temperature is known as sink. (Examples : River, Sea)

 From Kelvin-Planck statement it is clear that for any system to operate in a cycle and to give out work continuously it should interact with a minimum of two reservoirs at different temperatures. The system will receive heat from the high temperature reservoir and reject heat to the low temperature reservoir. Such devices are known as heat engines. Performance (or) Efficiency of a heat engine can be expressed as the ratio of desired output to the required input. In a heat engine the desired output is net work output and the required input is total heat input.



From first law of thermodynamics



**Clausius statement :** Unaided by an external agency heat can not be transferred from a body at lowertemperature to a body at higher temperature*.*

  Devices that are used to transfer heat from a body at lower temperature to a body at higher temperature are known as refrigerators (or) heat pumps. If the high temperature side is atmosphere it is a refrigerator. If the low temperature side is atmosphere it is known as a heat pump. The performance index here is called coefficient of performance (COP). In refrigerator (and heat pumps) the performance is the ratio of two independent parameters and hence the possibility of getting the value more than unity is always there. But the term efficiency is restricted to a maximum of unity. Hence the term efficiency is not used here.



COP=Q/W

Taking work as external agency, for refrigerators (Figure 4.2)

From first law

QW

Q1 Q2 W

*COP* *Q*2 / *Q*1 – *Q*2





Similarly for a heat pumps (Figure 4.3)



**Equivalence of Kelvin-Planck and Clausius Statements**

  The Clausius and Kelvin-Planck statements of the second law are entirely equivalent. This equivalence can be demonstrated by showing that the violation of either statement can result in violation of the other one.

Referring to Figure 4.4(a) the device marked Clausius violator is pumping Q1 amount of heat from a low temperature reservoir at T1 to a high temperature reservoir at T2 without the aid of any external agency. This is an impossible arrangement.

  If such an arrangement is possible it would also violate Kelvin-Planck statement. Let a heat engine operating between the same reservoirs at T2 and T1 take in Q2 as heat input at T2. It converts a part of this heat into work and rejects heat Q3to the sink at T1. Since the Clausius violator is rejecting the same quantity Q2at T2, it can be supplied directly into the heat engine so that the reservoir at T2 can be eliminated. This combination as shown in Figure 4.4 (b) is producing continuous work with a single reservoir at T1. Hence it violates the Kelvin-Planck statement.



**Figure 4.4 Illustration of the equivalence of Clausius and Kelvin-Planck’s   statemen**



Referring to Figure 4.5 a Kelvin-planck violator is converting all heat QH taken from the reservoir at TH into work. If such an impossible heat engine is assumed to exist it will violate the Clausius statement. Consider a refrigerator pumping QL heat from the low temperature reservoir at TL to the reservoir at higher temperature TH. Combined with the Kelvin-Planck violator, the arrangement is pumping QL heat from TL to TH, without any external agency. Hence it violate the Clausius statement.

**ENTROPY**

  The first law of thermodynamics deals with the property energy and the conservation of energy. The second law introduced in the previous chapter, leads to the definition of a new property called entropy. Entropy is defined in terms of a calculus operation, and no direct physical picture of it can be given. In this chapter, Clausius inequality, which forms the basis for the definition of entropy will be discussed first. It will be followed by the discussion of entropy changes that take place during various processes for different working fluids. Finally, the reversible steady-flow work and the isentropic efficiencies of various engineering devices such as turbine and compressors will be discussed.

**The Clausius Inequality**

Consider two heat engines operating between two reservoirs kept at temperature TH and TL as shown in the Figure 5.1. Of the two heat engines, one is reversible and the other is irreversible.





As discussed earlier, the work output from the irreversible engine should be less than that of the reversible engine for the same heat input QH. Therefore QL,Irrev will be greater than QL,Rev . Let us define

QL, Irrev QL, Rev Dq



This is known as *Clausius inequality*.

 Clausius inequality forms the basis for the definition of a new property known as entropy.

Consider a system taken from state 1 to state 2 along a reversible path A as shown in Figure 5.2. Let the system be brought back to the initial state 1 from state 2 along a reversible path B. Now the system has completed one cycle. Applying Clausius inequality we get



Instead of taking the system from state2 to state1 along B, consider another reversible path C. Then for this cycle 1-A-2-C-1, applying Clausius inequality :



Comparing 5.2 & 5.3

Hence, it can be concluded that the quantity is a point function, independent of the path followed. Therefore it is a property of the system. Using the symbol S for entropy we can write

upon integration we get



For a reversible process.

**Temperature - Entropy diagram**

 In a T-s diagram consider a strip of thickness ds with mean height T as shown in Figure 5.4. Then Tds gives the area of the strip.

 For a reversible process the elemental heat transfer

dQ Tds Area of the strip

 To get the total heat transfer the above equation should be integrated between the limits 1 and 2, so that, we get

 This is equivalent to the area under a curve representing the process in a T-S diagram as shown in the Fig 5.4.

 ***Note:*** *For an isothermal process S2**S1**.*

 *For reversible adiabatic process S2 S1* *0.*

**Change in Entropy**

 **a)**  **Solids and Liquids**

 Change in entropy

 Where  dq du+ pdv

 For solids and liquids

 pdv 0

Where c- is the specific heat

**b)**      **For ideal gases change in entropy**

Substituting

 du CvdT

  We get ,Upon integration

 Substituting dh CpdT

 and We get Upon integration

**Principle of Increase in Entropy**

 Applying Clausius inequality,

 For an isolated system undergoing a process

  Consider a system interacting with its surroundings. Let the system and its surroundings are included in a boundary forming an isolated system. Since all the reactions are taking place within the combined system, we can express

 or

  Whenever a process occurs entropy of the universe (System plus surroundings) will increase if it is irreversible and remain constant if it is reversible. Since all the processes in practice are irreversible, entropy of universe always increases

ie.,     (s)universe>0

 This is known as principle of increase of entropy.

 **Adiabatic Efficiency of Compressors and Turbines**

In steady flow compressors and turbines reversible adiabatic process is assumed to be the ideal process. But due to the irreversibilities caused by friction between the flowing fluid and impellers, the process is not reversible though it is adiabatic. Percentage deviation of this process from the ideal process is expressed in terms of adiabatic efficiency.

 **(a) Compressors :**

 Since compressors are work consuming devices actual work required is more than ideal work. For compressors handling ideal gases

 **(b) Turbines :**

 In turbine due to irreversibilities the actual work output is less than the isentropic work.

**AVAILABLE ENERGY, AVAILABILITY AND IRREVERSIBILITY**

From second law of thermodynamics we found that complete conversion of heat into work is not possible in a continuous process. Also it has been proved that the most efficient cycle to produce work is a reversible power cycle (Carnot cycle). Even in carnot cycle, the efficiency of conversion can never be

unity and hence to establish a comparison of the work-energy conversion in actual processes, the maximum theoretical work obtainable with respect to some datum must be determined. This chapter is dedicated for this objective.

**Available and Unavailable Energy**

The energy content of a system can be divided into two parts

             Available energy, which under ideal conditions may be completely converted into work

 Unavailable energy which is usually rejected as waste.

Consider Q units of heat energy available at a temperature T. Available part of energy can be obtained by assuming that the heat is supplied to a Carnot engine. Work obtained from the carnot engine



quantities can be represented as shown in the fig 6.1. The term T0 is the ambient temperature. Hence it can be concluded that the available and unavailable part of energy content of a system depends on the ambient conditions also.

 **Reversible Work In A Non-flow Process**

From first law of thermodynamics

Qsys W=U2U1 ...6.1

From second law of thermodynamics for a reversible process



This is also the maximum work in the process.

 For a closed system, when undergoing change in volume, the work done against the atmospheric pressure:



**Reversible Work In A Steady-state Control Volume**

Steady flow energy equation for a constant volume is





From eqn 6.6 neglecting kinetic and potential energy changes



**Availability**

  The maximum useful work that can be obtained from the system such that the system comes to a dead state, while exchanging heat only with the surroundings, is known as availability of the system. Here the term dead state means a state where the system is in thermal and mechanical equilibrium with the surroundings.

 Therefore for a closed system availability can be expressed as

U Uo po V Vo To SSo 

 similarly for an open system

 H Ho To SSo 

 In steady flow systems the exit conditions are assumed to be in equilibrium with the surroundings. The change in availability of a system when it moves from one state to another can be given as:

or a closed system

12 U1 U 2 po V1 V2 To S1 S2 ) ...6.10

for an open system

****

**Availability Change Involving Heat Exchange with Reservoirs**

Consider a system undergoing a change of state while interacting with a reservoir kept at TR and atmosphere at pressure po and temperature To. Net heat transfer to the system



Qnet= QR-QO.

From first law of thermodynamics

Qnet- Wrev=U2-U1 ...6.12

From second law of thermodynamics, assuming the process to be reversible

(s)Res+(s)atm+(s)sys=0



The negative sign for QR shows that the heat is removed from the reservoir.

 By rearranging We get

 Net heat transferred



**Irreversibility**

*Work obtained in an irreversible process will always be less than that of a reversible process. This difference is termed as irreversibility (i.e) the difference between the reversible work and the actual work for a given change of state of a system is called irreversibility.*

I=Wrev  Wact

Let a stationary closed system receiving Q kJ of heat is giving out Wact kJ of work. From first law of thermodynamics.



Since (s)universe will be positive for an irreversible flow, irreversibility will be zero for a reversible process and will never be negative

I 0.

Similarly for a steady flow system



**REAL GAS**

 **Real gas**, as opposed to a Perfect or Ideal Gas, effects refers to anassumption base where the following are taken into account:

•Compressibility effects

•Variable heat capacity

 •Van der Waals forces

•Non-equilibrium thermodynamic effects

 •Issues with molecular dissociation and elementary reactions with variable composition.

  For most applications, such a detailed analysis is "over-kill" and the ideal gas approximation is used. Real-gas models have to be used near condensation point of gases, near critical point, at very high pressures, and in several other less u

 **VAN DER WAALS MODELISATION**

  Real gases are often modeled by taking into account their molar weight and molar volume



Where P is the pressure, T is the temperature, R the ideal gas constant, and Vm the molar volume. a and b are parameters that are determined empirically for each gas, but are sometimes estimated from their critical temperature (Tc) and critical pressure (Pc) using these relations:



**REDLICH–KWONG MODELISATION**

  The Redlich–Kwong equation is another two-parameters equation that is used to modelize real gases. It is almost always more accurate than the Van der Waals equation, and often more accurate than some equation with more than two parameters. The equation is



**THERMODYNAMICS RELATIONS**



**Maxwell**     **relations.**

The Maxwell’s equations relate entro properties p,v and T for pure simple compressible substances.

From first law of thermodynamics,

Q = W +  U

Rearranging the parameters

Q =  U + W since [ds =            , W = pdv ]

 Tds = du +pdv

du = Tds –pdv     ----------- (1)

We know that, h = u + pv

dh = du + d(pv)

= du + vdp + pdv          ----------- (2)

Substituting the value du in equation (2),

dh = Tds + pdv + vdp –pdv

dh = Tds + vdp    ----------- (3)

By   Helmotz’s   function,

a = u –Ts

da = du –d(Ts)

= du –Tds –sdT             ----------- (4)

Substituting the values of du in equation (4),

da = Tds –pdv –Tds –sdT

T = –pdv –sdT     ----------- (5)

By Gibbs functions,

G = h –Ts

dg = dh –d(Ts)

dg = dh –Tds –sdT        ----------- (6)

Substituting the value of dh in equation (6),

 So, dg becomes

 dg = Tds + vdp –Tds –sdT

 dg = vdp –sdT      ----------- (7)

 By inverse exact differential we can write equation (1) as, du = Tds –pdv

 ----------- (8)

Similarly, equation (3) can be written as, dh = Tds + vdp



Similarly, equation (5) can be written as,





**Tds relations in terms of temperature and pressure changes and temperature and volume changes.**

 The entropy (s) of pure substance can be expressed as a function of temperature (T) and pressure (p).

We know that,

 

This is known as the first form of entropy equation or the first Tds equation. By considering the entropy of a pure substance as a function of temperature and specific volume,

i.e.    s = f(T,v)



From the Maxwell Equations, we know that



This is known as the second form of entropy equation or the second Tds equation

**The third law of thermodynamics states that:**

“The entropy of all the perfect crystalline solids is zeros at absolute zero temperature”. The third law of thermodynamics is also referred to as Nernst law. It provides the basis for the calculation of absolute entropies of the substances.

Mathematically,

**LimT –>0 S = 0**

If the entropy is zero at temperature T = o, then this law states that the absolute entropy Sab of a substance at temperature T and pressure P is expressed by the followingexpression:

SabT∫0 (δQ) rev / T

**Importance of third law of thermodynamics is given below:**

1) It helps in calculating the thermodynamic properties.

2) It is helpful in measuring chemical affinity. Because of this it is known as Nernst theorem.

3) It explains the behavior of solids at very low temperature.

4) It helps in analyzing chemical and phase equilibrium.