UNIT 2

Basic Concepts of Thermodynamics

After going through this unit, the reader would be able to understand the following:
- (1) Thermodynamic system and its types.
- (2) Thermodynamic properties.
- (3) Quasi-static process.
- (4) Zeroth, I, II and III laws of thermodynamics.
- (5) Concept of entropy.

2.1 BASIC CONCEPTS

— Thermodynamics is the science of energy and entropy.
— Thermodynamics is the science that deals with heat and work and the properties of substances that bear a relation to heat and work.
— The basis of thermodynamics is experimental evidence and observation. These observations have been formalized into certain basic laws, which are known as zeroth, first, second and third laws of thermodynamics.

Definitions

Thermodynamic System: It is a three-dimensional region of space or an amount of matter which is under consideration. It is enclosed by an imaginary surface or real surface which may be at rest or in motion, and can change its size or shape. Everything outside the arbitrarily selected boundaries of the system is called surrounding.

Universe: Combination of system and surrounding is called universe.

Open System: The system which can exchange both mass and energy with its surroundings is called an open system. The region of space for observation is described as control volume. The boundary of control volume is called control surface. In such a system, flow type of processes occur. For example, turbine, boiler pump, compressor, condenser, nozzle, diffuser, etc.

Extensive Property: Properties which depends on the mass of the system or in other words, value for the whole system is the sum of its values for the various subsystems or parts. Examples: Volume (V), Energy (E).

Intensive Property: These properties have values that are independent of the size or amount of mass of the system. These have fixed value. If a given phase system in equilibrium is divided into n parts, then the value of given intensive property will be the same for each of the subsystems. Examples: Temperature, pressure, density velocity and chemical concentration, etc.

If extensive property like Energy (E) of overall system is divided by the mass (m) of overall system, the resulting property is called specific property. $e = E/m$. A specific property is an intensive property.

State: When all the properties of a system have definite values, then the system is said to exist at a definite state. Properties are the coordinates to describe the state of a system. Any operation in which one or more of the properties of a system changes is called a change of state.

Path: The succession of states passed through during a change of state is called the path of the change of state.

Process: When the path is completely specified, the change of state is called a process, e.g. constant temperture process (isothermal process), constant pressure process (isobaric process).

Cycle: A thermodynamic cycle is defined as a series of state change such that the final state is identical with the initial state.

Phase: A quantity of matter homogeneous throughout in chemical composition and physical stucture is called a phase. Every substance can exist in any one of the three phases:
   (1) Solid
   (2) Liquid
   (3) Gas

Homogeneous System: A system consisting of a single phase is called a homogeneous system.

Heterogeneous System: A system consisting of more than one phase is called a heterogeneous system.

Thermodynamic Equilibrium: If the system is isolated from its surroundings and no change in its macroscopic properties occur, then it is called in thermodynamic equilibrium. A system will be in state of thermodynamic equilibrium if the condition for the following three types of equilibrium are satisfied:
   (a) Mechanical Equilibrium
   (b) Chemical Equilibrium
   (c) Thermal Equilibrium

Temperature and Temperature Scale

Temperature scale is referred to a thermometer for measuring inequality of temperature. To construct a thermometer two reference points are chosen, namely ice point and steam point.

Generally, two scales are used, namely Celsius and Fahrenheit. The Celsius scale (often referred to as the centigrade scale) is named after Anders Celsius (1701–44) and Fahrenheit scale is named after Daniel Gabriel Fahrenheit (1686–1736). The lower fixed point (ice point) is the temperature at which pure ice melts. The upper fixed point (steam point) is the temperature at which pure water boils. These are known as freezing point and boiling point respectively. These are 0°C and 100°C in the celsius scale and 32°F and 212°F in the Fahrenheit scale. Following equation is used to derive the relation between these two scales:

$$\frac{C - \theta_{ice}}{\theta_{steam} - \theta_{ice}} = \frac{F - \theta_{ice}}{\theta_{steam} - \theta_{ice}}$$

or
$$\frac{C - 0}{100 - 0} = \frac{F - 32}{212 - 32}$$

or
$$\frac{C}{100} = \frac{F - 32}{180}$$

$$\frac{C}{5} = \frac{F - 32}{9}$$

Likewise we can get relations between different scales:

(1) To convert Celsius to Fahrenheit

$$F = \frac{9}{5}C + 32$$

(2) To convert Fahrenheit to Celsius

$$C = \frac{5}{9}(F - 32)$$

(3) To convert Celsius to Kelvin

$$k = C + 273$$

(4) To convert Fahrenheit to Rankine

$$R = F + 460$$

(5) To convert Kelvin to Rankine

$$R = \frac{9}{5}k$$

(6) To convert Rankine to Kelvin

$$k = \frac{5}{9}R.$$

Comparison to Temperature Scale

Scale	Fahrenheit °F	Centigrade °C	Kelvin K	Rankine °R
(i) Steam point	212	100	375.15	671.67
(ii) Triple point	32.02	.01	273.16	491.69
(iii) Ice point	32	0	−273.15	491.67
(iv) Absolute zero	−459.67	−273.15	0	0

Devices used for the measurement of temperature:
(1) Fluid thermometers.
  (a) Mercury in glass—thermometers.
  (b) Beckman thermometer—It can measure temperature rise of usually 6°C with an accuracy of 0.01°C.
  (c) The constant volume gas thermometer.

(2) Temperature gauge using fluids.
  (a) Temperature gauge

(3) Dimetallic strip method.

(4) Pyrometers
  (a) Thermocouples—measured due to Peltier and Thomson effect. The thermocouples used are:
    Chromel (+)   Alumel (−)
    Iron (+)   Constantan (−)
    Copper (+)   Constantan (−)
    Chromel (+)   Copel (−)
  (b) The resistance thermometer—the equation used

$$R = R_0 (1 + \alpha t)$$

  where R_0 = original resistance.
       α = coefficient of increase of resistance with temperature t
    (i) The radial pyrometer.
    (ii) The fusion pyrometer.
    (iii) Thermal points.

2.4 INTRODUCTION TO FIRST LAW

The first law of thermodynamics was proposed by Joule in 1851 known as the principle of conservation of energy. Prior to James P Joule (1818–90) heat was considered an invisible fluid flowing from a body of higher calorie to a body of lower calorie and it was known as calorie theory of heat. It was Joule who first established that heat is a form of energy. During 1840–49 he conducted several experiments for the formulation of the first law of thermodynamics. Work was transferred to the measured mass of water kept in an adiabatic vessel by means of a paddle wheel driven by the falling of a weight. The rise in temperature of the water was recorded by a thermometer. Let the initial temperature of the water in the vessel be T_1. The paddle wheel work increased the water temperature to T_2. The cover was then removed and bath was allowed to return to its original temperature T_1. The system thus executed a cycle which consisted of a definite amount of work input W_{1-2} into the system followed by the transfer of an amount of work W_{1-2} into transfer of an amount of heat Q_{2-1} from the system. Joule repeated this experiment for different weights falling through different distances and measured each temperature rise. In each and every case, Joule found that work and heat have a constant relation. This constant of proportionality is called Joule's constant or the mechanical equivalent of heat (J).
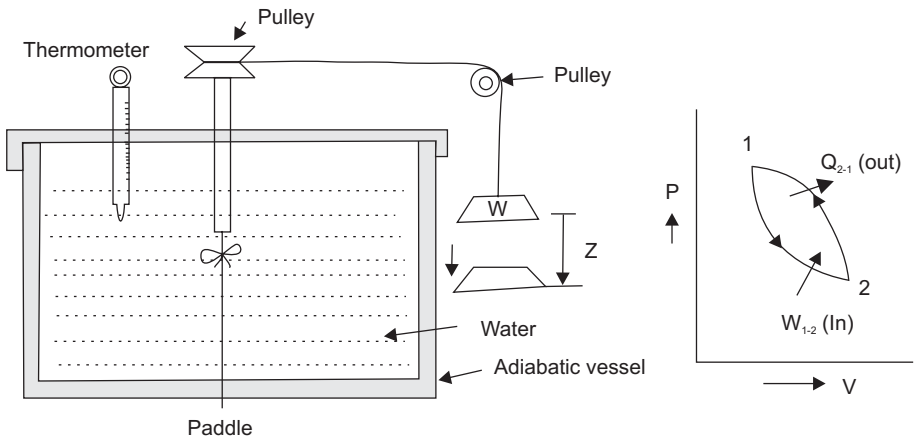
$$\text{Work/Heat} = \text{Constant (J)}$$

Fig. 2.4: Diagram explaining 1st law.

If the cycle involves several work and heat transfers, the result is the same and can be written as:

$$\Sigma W_{cycle} = I\Sigma Q_{cycle}$$

Statement: 1st law of thermodynamics: If the system undergoes a cyclic change of state, then the algebraic sum of the work delivered to the surroundings is proportional to the algebraic sum of heat taken from the surroundings.

E = Sum of microscopic and macroscopic modes of energy.

$$E = U + PE + KE$$

PE is bulk potential energy, *KE* is bulk kinetic energy and *U* is the total internal energy of the system.

In an ideal gas, there are no intermolecular forces of attraction and repulsion and the internal energy depends only on temperature. Thus,

$$U = f(T) \text{ only for an ideal gas.}$$

A system can possess other forms of energies also, like magnetic energy, electrical energy and surface (tension) energy. In the absence of these forms; the total energy *E* of a system is given by:

$$E = U + PE + KE \tag{5}$$

In the absence of motion and gravity, $KE = 0$ and $PE = 0$,

$$E = U$$

Therefore, equation 5 becomes

$$\delta Q - \delta W = dE$$

$\delta Q - \delta W$ is independent of path and depends upon end states only, internal energy

U which is equal to $\int(\delta Q - \delta W)$ is also independent of path and hence a property of the system.

Internal Energy: Internal energy can be defined as a form of stored energy in a system in the absence of magnetism, electricity, capillarity, surface tension, motion and gravity.

2.5 LIMITATIONS OF THE FIRST LAW AND INTRODUCTION TO THE SECOND LAW

It is a common experience that while work is very easily converted into heat (by rubbing both hands we generate heat) but heat cannot be easily converted into work. The first law, however, places no restriction on the direction of flow of heat and work. For example, in the case of disc brakes, when it is stopped by friction pad, the pad as well as disc gets heated up, because the KE lost by the disc is converted into heat energy. The first law of thermodynamics would be equally satisfied if the brakes were to cool off and give back its internal energy to disc causing it to resume its rotation again. This may, however, never occur. The action of the brake in stopping the disc by friction is irreversible process. Thus, we can conclude that there exists a directional law which imposes limitation on energy transformation.

Statement of second law also called **Kelvin-Planck statement**. "It is impossible to construct an engine which will work in a complete cycle and produce no other

effect except the rising of a weight (the production of work) and the exchange of heat with a single reservoir".

Thus, according to this law, an engine E as shown in figure working on cyclic process (which means that there is no change in the internal energy for the complete cycle) cannot simply receive an amount of heat, say Q from a heat source and deliver work W such that W is equal to Q. Such an engine would satisfy the first law of thermodynamics but violate the second law.
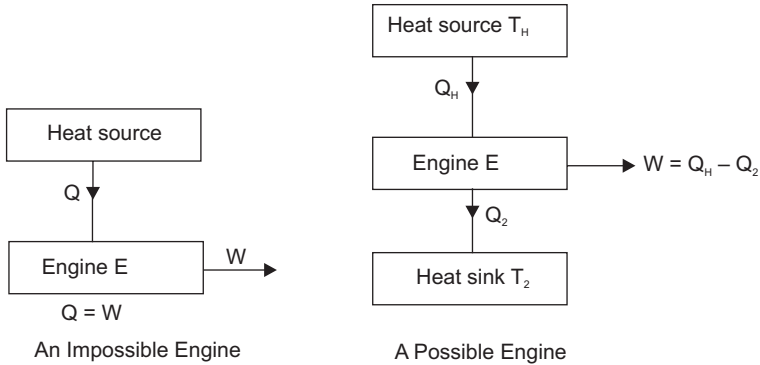

Fig. 2.6

Thus, a practical engine must reject some of the heat which it receives. An engine is a device to convert heat into work whereas a heat pump is a device to pump (transfer) heat from a lower temperature to a higher temperature while operating in a cycle.

Clausius' statement on the second law: "It is impossible to construct a heat pump which will work in a complete cycle and produce no effect except to transfer heat from cold reservoir to a hot reservoir". Or in other words, it is stated as "heat itself cannot flow from a cold to a hot body".

Perpetual motion machine of second kind: A heat engine that exchanges heat with a single body in an equilibrium state and produces work without creating any other effect is called perpetual motion machine of second kind. Obviously, such a machine is impossible. Therefore, based on this concept there is another statement of second law. "Perpetual motion machine of the second kind is an impossibility".
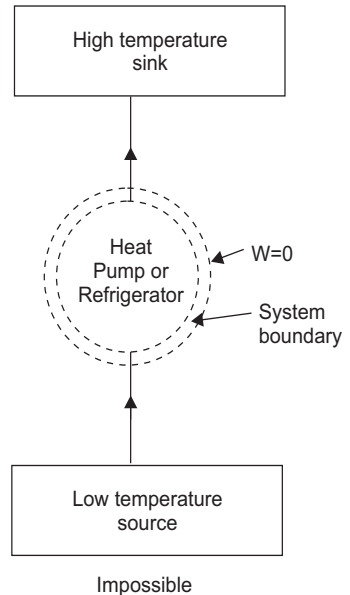
Fig. 2.7: Clausius' statement's Explanation.

Process (4–1): Reversible adiabatic compression. Work is supplied for compression by an external source in a device.

$$\text{Work done} = \frac{P_4 V_4 - P_1 V_1}{\gamma - 1}$$

Network Done = Heat supplied – Heat rejected

$$Q_H - Q_L = mR(T_H - T_L)\ln r$$

$$\text{Thermal efficiency of Carnot cycle} = \frac{\text{Work done per cycle}}{\text{Heat supplied per cycle}}$$

$$= \frac{mR(T_H - T_L)\ln r}{mRT_H \ln r} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}$$

$$\eta_{\text{carnot}} = \left[1 - \frac{T_L}{T_H} \right].$$

$$\eta_{\text{carnot}} = \frac{T_{\max} - T_{\min}}{T_{\max}}$$

Thus, Carnot efficiency depends only on temperature difference of source and sink and is independent of working substance.

Example
Due to metallurgical limit of boiler tube, piston cylinder and turbine blades maximum temperature of working fluid should not exceed 660°C. Temperature at which heat is rejected from sink should be more than atmospheric temperature. In India, an average atmospheric temperature is considered to be 25°C. Let us consider that the heat rejection temperature is about 45°C (more than 25°C for better heat tansfer). So, maximum value of Carnot efficiency would be about:

$$\eta_{\text{carnot}} = 1 - \frac{45 + 273}{660 + 273} = 1 - \frac{318}{933} = 1 - .34 = .659$$

That is, Carnot efficiency should not exceed 65.9%.

Carnot efficiency gives the maximum value of efficiency which can be acheived by any engine operating between the same temperature limits.

Reversed Carnot Cycle: It is an ideal cycle for refrigerator and heat pumps. The cycle consists of four processes which are as follows:
Process (1–2):   Reversible adiabatic expansion in an expanding device.

Process (2–3):   Reversible isothermal heat absorption from low temperature source.

Process (3–4):   Reversible adiabatic compression in a compressor.

Process (4–1):   Reversible isothermal heat rejection to high temperature sink.
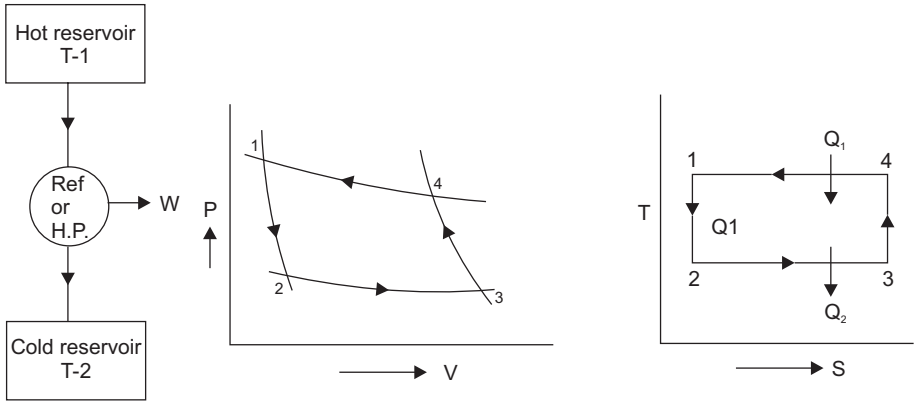
Fig. 2.9

Performance of refrigerator and heat pump:

$$(COP)_{ref} = \frac{\text{Heat abstracted from cold reservior}}{\text{Work supplied}}$$

$$(COP)_{H.P.} = \frac{\text{Heat rejected to hot sink (surroundings)}}{\text{Work supplied}}$$

$$(COP)_{ref} = \frac{T_{min}}{T_{max} - T_{min}}$$

$$(COP)_{H.P.} = \frac{T_{max}}{T_{max} - T_{min}}$$

Carnot Theorem: No heat engine working between two thermal reservoirs with fixed temperatures can be more efficient than a reversible engine operating between same thermal reservoirs.

The proof is as follows:

Let there be a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. Imagine a reversible engine R taking 100 kJ from the heat reservoir and converting 60 kJ into work and rejecting 40 kJ to the cold reservoir, the engine efficiency being 60%. If this engine is reversed, it will take 60 kJ to drive it

another 40 kJ will be taken from the cold reservoir and 100 kJ will be delivered to the hot reservoir.

Assume an irreversible engine I having efficiency greater than that of the reversible engine say 75% and driving the reversible engine without any losses. Now for the same 60 kJ work done heat taken by irreversible engine = 60/0.75 = 80 kcal from the hot reservoir and heat rejected to the cold reservoir = (80–60) = 20 kJ. In this system, reversible engine delivers (100–80) = 20 kJ heat more to hot reservoir than the irreversible engine takes from it. Also reversible engine takes (40–20) = 20 kJ heat more from the cold reservoir than the irreversible engine delivers to it and this heat is being pumped from the cold reservoir to the hot reservoir without any external power which is contrary to the second law of thermodynamics. Hence, the assumption that irreversible engine is more efficient is wrong.
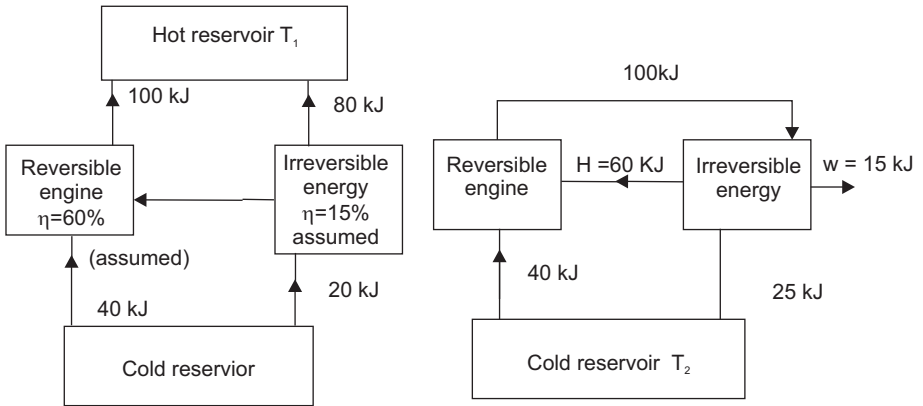

Fig. 2.10

The assumption of higher efficiency for irreversible engine contradicts the second law.
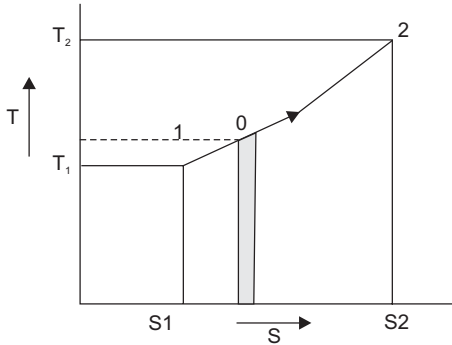
2.7 ENTROPY

Entropy of a substance is a property which increases with the addition of heat. Entropy itself cannot be defined but change of entropy can be defined. Mathematically, in a reversible process, the increase of entropy when multiplied by the absolute temperature, gives the heat received by the fluid from an external source.

The change of entropy with temperature is shown on a diagram known as Temperature entropy (T-S) diagram.

The initial condition of a gas receiving heat is denoted by point 1 while its final state be represented by point 2. Considering any point 0 on the curve, a small addition of heat dQ under reversible conditions increases entropy by dS. If T is the

absolute temperature at this instant, by the mathematical definition of entropy, we get $dQ_{rev} = Tds \ ds = \dfrac{dQ_{rev}}{T}$ from figure. Tds is the area under the curve during the change of entropy ds.

$$Q = \int_{T_1}^{T_2} Tds = \text{area under the curve 12}$$

Fig. 2.11: Temperature-entropy diagram

Thus, for any reversible heating and expansion of a gas, the area under the curve, T-S diagram gives the total heat absorbed. The change in entropy is also equal to maximum amount of work obtainable for a unit temperature drop in a heat engine. The maximum work dW obtainable from an amount of heat dQ is given by the Carnot efficiency.

$$dW = dQ \times \frac{(T_1 - T_2)}{T_1}$$

If temperature drop (T1–T2) is unity:

$$dW = \frac{dQ}{T} = \text{change of entropy } dS$$

Thus, the change of entropy may be regarded as a measure of the rate of availability of heat for transformation into work.

Physical Concept of Entropy

The entropy of a substance is a real physical quantity defining the state of the body and can be easily evaluated for a solid or a perfect gas except for an additive constant representing the entropy at the absolute zero.

Entropy can be viewed as a measure of molecular disorder, or molecular randomness. As a system becomes more disordered, the positions of the molecules

becomes less predictible and the entropy increases. Thus, it is not surprising that the entropy of a substance is lowest in the solid phase and highest in the gas phase. In the solid phase, the molecules of a substance continually oscillate about their equilibrium positions, but they cannot move relative to each other and their positions at any instant can be predicted with good certainty. In the gas phase, however, the molecules move about at random, collide with each other, and change direction, making it extremely difficult to predict accurately, the microscopic state of a system at any instant. Associated with this molecular chaos is a high value of entropy.

Heat is, in essence, a form of disorganized energy, and some disorganization (entropy) will flow with heat. As a result, the entropy and the level of molecular disorder or randomness of the hot body will decrease with the entropy and the level of molecular disorder of the cold body will increase. The second law requires that the increase in entropy of the cold body be greater than the decrease in entropy of the hot body and thus, the net entropy of the combined system (the cold body and hot body) increases. That is, the combined system is at a state of greater disorder at the final state.

Clausius Inequality

When any closed system undergoes a cyclic process, the sum of all $(\delta q/T)$ terms at the system boundary for each differential element of the process will always be equal to or less than zero. Thus,

$$\oint \frac{\delta q}{T} \leq \text{for any cyclic process (possible) (Clausius' inequality)}$$

If $\oint \frac{dQ}{T} = 0,$ the cycle is reversible $ds = 0$

$\oint \frac{dQ}{T} < 0$, the cycle is irreversible and possible $ds > 0$

$\oint \frac{dQ}{T} > 0,$ the cycle is impossible

2.8 THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics often referred to as the Nernst law, provides the basic for the calculation of absolute entropy of the substances.

Third Law Statement

The entropy of all perfect crystalline solid is zero at absolute zero temperature.

The absolute zero temperature, O.K. or OR, exists in the thermodynamic temperature scale. This correponds to –273.15°C and –459.67°F on the celcius and fahernheit scale respectively.

In practice one can never achieve absolute zero temperature as it is impossible but temperatures very close to it have been attained due to perfect insulation.

Comparison of first and second law of thermodynamics.

First Law	Second Law
1. According to the first law heat and work are of same quality indicating 100% efficiency of a cyclic engine	Work is considered to be a high grade energy where as heat as a low grade energy
2. Results in the definition of the extensive property; internal energy	Results in the definition of the extensive property; entropy
3. States that energy of an isolated system can neither be created nor destroyed	States that entropy of an isolated system cannot be destroyed but it can be created
4. Energy of the universe is constant	The entropy of the universe increases towards a maximum
5. Energy is conserved in every real process	Energy is degraded in every real process

SOLVED PROBLEMS

Problem 1
A freezer is to be maintained at a temperature of 238 K when the ambient temperature is 306 K. In order to maintain the freezer box at 238 K it is necessary to remove heat from it at the rate of 2460 J/sec. What is the maximum possible coefficient of performance of the freezer and what is the minimum power that must be supplied to the freezer.

Solution
The maximum coeffcient of performance is obtained when the freezer operates reversibily.

Max COP of a refrigerator

$$= \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} = \frac{238}{306} = 3.5 \textbf{ Ans.}$$

But $Q_2 = 2460$ J/S and $Q_1 - Q_2 = W$

$$\frac{2460}{W} = 3.5 \text{ or } W = \frac{2460}{3.5} = 702.8 \text{ J/S}$$

$$= 702.8 \text{ } W \text{ } \textbf{Ans.}$$

Problem 2

An inventor claims to have developed a cyclic engine which exchanges heat with reservoirs at 130°C and –40°C. It receives onlyu 2100 kJ/min of heat and develops 17.66 kW Is his claim feasible?

Solution

The maximum efficiency of a heat engine can be equal to that of carnot engine

$$\eta_{max} = \frac{T_1 - T_2}{T_1}$$

$$= \frac{(273 + 130) - (273 - 40)}{(273 + 130)} = \frac{433 - 239}{403}$$

$$= 0.422 \text{ or } 42.2\%$$

The claimed efficiency = work output/heat input

$$= \frac{17.66}{2100/60} = 0.50$$

$$= 50.45\%$$

The claimed efficiency is even greater than the carnot engine efficiency which is not possible. Therefore the claim is not feasible.

Problem 3

A heat engine works between hot and cold reservoirs at 556 K and 278 K. the engine reservoirs at 556 K and 278 K. The engine receives 278 kJ/sec of heat. The following results were reported
   (i) 70 kJ/sec of heat was rejected
   (ii) 139 kJ/sec of heat was rejected
   (iii) 208 kJ/sec of heat was rejected
Indicate which of the results shows a reversible cycle, irreversible cycle or impossible cycle.

Solution

We know that

$$\oint \frac{dQ}{T} = 0 \text{ for a reversible cycle}$$

$$\oint \frac{dQ}{T} = 0 \text{ for an irreversible cycle}$$

$$\oint \frac{dQ}{T} > 0 \text{ is impossible}$$

Now taking three cases we have

Since
$$\oint \frac{dQ}{T} = \oint_{\substack{heat \\ added}} \frac{dQ}{T} + \oint_{\substack{heat \\ rejected}} \frac{dQ}{T}$$

∴ for case (i)
$$\oint \frac{dQ}{T} = \frac{278}{556} - \frac{70}{278} = 0.248$$

This is positive so case (i) is impossible

Case (ii)
$$\oint \frac{dQ}{T} = \frac{278}{556} - \frac{139}{278} = 0$$

∴ the cycle is reversible

Case (iii)
$$\oint \frac{dQ}{T} = \frac{278}{556} - \frac{208}{278} = 0.248$$

This is negative

∴ The cycle is irreversible

Problem 4

Q4(a). In a certain reversible process the rate of heat transfer to the system per unit temperature is given by $\frac{dQ}{dT} = 1.05$ kJ/K. Find the increase in entropy of the system. If its temperature rises from 300°K to 400°K. Also find the change in specific entropy if mass of system in 2 kg.

(b). In a second process between the same and states the temperature rise is obtained by stirring accompanied by a heat addition half as great as in case (a) find the increase in entropy in the case.

2. Intensive property of a system is one whose value.
    (a) depends on the mass of the system like volume
    (b) does not depend on the mass of the system, like temperature pressure etc.
    (c) is not dependent on the path followed but on the state
    (d) is dependent on the path followed and not on the state
3. Heat and work are
    (a) point functions
    (b) system properties
    (c) path functions
    (d) intensive properties
4. Which of the following is the property of a system
    (a) pressure and temperature
    (b) internal energy
    (c) volume and density
    (d) all of the above
5. Work done is zero for the following process
    (a) constant volume
    (b) free expansion
    (c) throttling
    (d) all of the above
6. Entropy change depends upon
    (a) heat transfer
    (b) mass transfer
    (c) change of temperature
    (d) thermodynamic state
7. First law of thermodynamics
    (a) enables to determine change in internal energy of the system
    (b) does not help to predict whether the system will or will not undergo a change
    (c) does not enable to determine change in entropy
    (d) all of the above
8. If a heat engine attains 100% thermal efficiency it violates
    (a) zeroth law of thermodynamics
    (b) first law of thermodynamics
    (c) second law of thermodynamics
    (d) all of the above laws
9. According to Clausius' statement
    (a) heat flow from hot substance to cold substance.
    (b) heat cannot flow from cold substance to hot substance.
    (c) heat can flow from cold substance to hot substance with the aid of external work.
    (d) none of the above

    (c) O°K
    (d) equal to inlet temperature

17. Calorie is a measure of
    (a) specific heat
    (b) quantity of heat
    (c) thermal capacity
    (d) entropy

18. The value of 1 bar in S.I. units is equal to
    (a) 1 N/m^2
    (b) 1 kN/m^2
    (c) $1 \times 10^4 \text{ N/m}^2$
    (d) $1 \times 10^5 \text{ N/m}^2$

19. Compressed air coming out from a punctured football
    (a) becomes hotter
    (b) becomes cooler
    (c) remains at the same temperature
    (d) attains atmospheric temperature

20. Which of the following cycles has maximum efficiency
    (a) Rankine
    (b) Stirling
    (c) Carnot
    (d) Brayton

21. Which of the following is extensive property?
    (a) entropy
    (b) internal energy
    (c) kinetic energy
    (d) all of the above

22. A process occurs spontaneously if its entropy
    (a) increases
    (b) decreases
    (c) remains same
    (d) becomes zero

23. Entropy is called the property of the system because
    (a) Its derivative is zero for any process.
    (b) It has some value at any two equilibrium states
    (c) It has a single value at each equilibrium state
    (d) It has a constant value at each equilibrium state

24. A reversible engine working between the temperatures limits of 600°K and 12°K receives 50 kJ of heat. The work done by the engine will be
    (a) 50 kJ
    (b) 100 kJ
    (c) 25 kJ
    (4) –25 kJ