

LECTURE NOTES

THERMODYNAMICS
(AME003)

B.TECH - SEMESTER-III

**PREPARED
BY**

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UNIT I

INTRODUCTION

THERMODYNAMICS

Thermodynamics is the science that deals with heat and work and those properties of substance that bear a relation to heat and work.

Thermodynamics is the study of the patterns of energy change. Most of this course will be concerned with understanding the patterns of energy change.

More specifically, thermodynamics deals with (a) energy conversion and (b) the direction of change.

Basis of thermodynamics is experimental observation. In that sense it is an empirical science. The principles of thermodynamics are summarized in the form of four laws known as zeroth, first, second, and the third laws of thermodynamics.

The zeroth law of thermodynamics deals with thermal equilibrium and provides a means of measuring temperature.

The first law of thermodynamics deals with the conservation of energy and introduces the concept of internal energy.

The second law of thermodynamics dictates the limits on the conversion of heat into work and provides the yard stick to measure the performance of various processes. It also tells whether a particular process is feasible or not and specifies the direction in which a process will proceed. As a consequence it also introduces the concept of entropy.

The third law defines the absolute zero of entropy.

Macroscopic and Microscopic Approaches:

Microscopic approach uses the statistical considerations and probability theory, where we deal with “average” for all particles under consideration. This is the approach used in the disciplines known as kinetic theory and statistical mechanics.

In the macroscopic point of view, of classical thermodynamics, one is concerned with the time-averaged influence of many molecules that can be perceived by the senses and measured by the instruments.

The pressure exerted by a gas is an example of this. It results from the change in momentum of the molecules, as they collide with the wall. Here we are not concerned with the actions of individual molecules but with the time-averaged force on a given area that can be measured by a pressure gage.

From the macroscopic point of view, we are always concerned with volumes that are very large compared to molecular dimensions, and therefore a system (to be defined next) contains many molecules, and this is called continuum.

The concept of continuum loses validity when the mean free path of molecules approaches the order of typical system dimensions.

System:

We introduce boundaries in our study called the system and surroundings.

The boundaries are set up in a way most conducive to understanding the energetics of what we're studying.

Defining the system and surroundings is arbitrary, but it becomes important when we consider the exchange of energy between the system and surroundings.

Two types of exchange can occur between system and surroundings: (1) energy exchange (heat, work, friction, radiation, etc.) and (2) matter exchange (movement of molecules across the boundary of the system and surroundings).

Based on the types of exchange which take place or don't take place, we will define three types of systems:

- isolated systems: no exchange of matter or energy
- closed systems: no exchange of matter but some exchange of energy
- open systems: exchange of both matter and energy

Control Volume

- Control volume is defined as a volume which encloses the matter and the device inside a control surface.
- Everything external to the control volume is the surroundings with the separation given by the control surface.
- The surface may be open or closed to mass flows and it may have flows from energy in terms of heat transfer and work across it.
- The boundaries may be moveable or stationary.
- In the case of a control surface that is closed to the mass flow, so that no mass can enter or escape the control volume, it is called a control mass containing same amount of matter at all times.

Property

- In thermodynamics a property is any characteristic of a system that is associated with the energy and can be quantitatively evaluated.
- The property of a system should have a definite value when the system is in a particular state.
- Thermodynamic property is a point function.
- Properties like volume of a system that depend on the mass of a system are called extensive properties.
- Properties like pressure or temperature which do not depend on the system mass are called intensive properties.
- The ratio of extensive property to the mass of the system are called specific properties and therefore become intensive properties.
- Substance can be found in three states of physical aggregation namely, solid, liquid and vapor which are called its phases.
- If the system consists of mixture of different phases, the phases are separated from each other by phase boundary.
- The thermodynamic properties change abruptly at the phase boundary, even though the intensive properties like temperature and pressure are identical.

Equilibrium

- When the property of a system is defined, it is understood that the system is in equilibrium.
- If a system is in thermal equilibrium, the temperature will be same throughout the system.
- If a system is in mechanical equilibrium, there is no tendency for the pressure to change. In a single phase system, if the concentration is uniform and there is no tendency for mass transfer or diffusion, the system is said to be in chemical equilibrium.
- A system which is simultaneously in thermal, mechanical, and chemical equilibrium is said to be in thermal equilibrium.

Process

A process is path followed by a system in reaching a given final state of equilibrium state starting from a specified initial state.

An actual process occurs only when the equilibrium state does not exist.

An ideal process can be defined in which the deviation from thermodynamic equilibrium is infinitesimal.

All the states the system passes through during a quasi-equilibrium process may be considered equilibrium states.

For non-equilibrium processes, we are limited to a description of the system before the process occurs and after the equilibrium is restored.

Several processes are described by the fact that one property remains constant.

The prefix iso- is used to describe such processes.

A process is said to be reversible if both the system and its surroundings can be restored to their respective initial states by reversing the direction of the process.

- Reversible: if the process happens slow enough to be reversed.
- Irreversible: if the process cannot be reversed (like most processes).

The main processes are

Isobaric: process done at constant pressure

- Isochoric: process done at constant volume
- Isothermal: process done at constant temperature
- Adiabatic: process where $q=0$
- Cyclic: process where initial state = final state

Internal Energy

- The molecule as a whole can move in x, y and z directions with respective components of velocities and hence possesses kinetic energy.
- There can be rotation of molecule about its center of mass and then the kinetic energy associated with rotation is called rotational energy.
- In addition the bond length undergoes change and the energy associated with it is called vibrational energy.
- The electron move around the nucleus and they possess a certain energy that is called electron energy.
- The microscopic modes of energy are due to the internal structure of the matter and hence sum of all microscopic modes of energy is called the internal energy.

Bulk kinetic energy (KE) and potential energy (PE) are considered separately and the other energy of control mass as a single property (U).

The total energy possessed by the body is given by:

$$E = KE + PE + U$$

Work

Whenever a system interacts with its surroundings, it can exchange energy in two ways- work and heat.

In mechanics, work is defined as the product of the force and the displacement in the direction of the force. Work done when a spring is compressed or extended: According to Hooke's law

Spring force = $-k(x - x_0)$

Where k is the spring constant, x_0 is the equilibrium position, and x is the final position. The negative sign shows that the direction of the spring force is opposite the direction of the displacement from x_0 . The external force is equal in magnitude but opposite in sign to the spring force, so External force (force of your hands) = $k(x - x_0)$.

Now, we want to calculate the work done when we stretch the spring from position 1 to position 2.

$$W = \int F dx = \int k(x - x_0) d(x - x_0) = \frac{1}{2} k [(x_2 - x_0)^2 - (x_1 - x_0)^2]$$

Work done when a volume is increased or decreased

Consider a gas in a container with a movable piston on top. If the gas expands, the piston moves out and work is done by the system on the surroundings. Alternatively, if the gas inside contracts, the piston moves in and work is done by the surroundings on the system. Why would the gas inside contract or expand?

It would if the external pressure, P_{ex} , and the internal pressure, P_{in} , were different. To calculate the work done in moving the piston, we know that the force = pressure times area and then work equals pressure times area times distance or work equals pressure times the change in volume. So, W = the integral of $(P_{ex}) dV$

The differential work done (dW) associated with a differential displacement (dl) is given by
 $dW = F dl$

For a piston cylinder assembly,

$$dW = F dl = PA (dl) = P dV$$

If the gas is allowed to expand reversibly from the initial pressure P to final pressure P , then the work done is given by

$$W = \int p \, dV$$

- The integral represents the area under the curve on a pressure versus volume diagram. Therefore the work depends on the path followed and work is a path function and hence not a property of the system.
- The above expression does not represent work in the case of an irreversible process.
- The thermodynamic definition of work is “ Work is said to be done by a system on the surrounding if the sole effect external to the system could be reduced to the raising of a mass through a distance”.

Heat

Heat like work, is a form of energy.

The energy transfer between a system and its surroundings is called heat if it occurs by virtue of the temperature difference across the boundary.

The two modes of energy transfer – work and heat- depend on the choice of the system.

Heat energy moves from a hotter body to a colder body upon contact of the two bodies.

If two bodies at different temperatures are allowed to remain in contact, the system of two bodies will eventually reach a thermal equilibrium (they will have the same temperature).

A body never contains heat. Rather heat is a transient phenomenon and can be identified as it crosses the boundary.

The State Postulate

The state of the system is described by its properties.

Once a sufficient number of properties are specified, the rest of the properties assume some values automatically.

The number of properties required to fix a state of a system is given by the state postulate:

The state of a simple compressible system is completely specified by two independent, intensive properties.

The system is called a simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.

The state postulate requires that the two properties specified be independent to fix the state.

Two properties are independent if one property can be varied while the other one is held constant.

Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system.

Thus, temperature and pressure are not sufficient to fix the state of a two-phase system.

Otherwise an additional property needs to be specified for each effect that is significant.

An additional property needs to be specified for each other effect that is significant.

Zeroth Law of Thermodynamics

We cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading.

Several properties of material changes with temperature in a repeatable and predictable way, and this forms the basis of accurate temperature measurement.

The commonly used mercury-in-glass thermometer for example, is based on the expansion of mercury with temperature.

Temperature is also measured by using several other temperature dependant properties.

Two bodies (eg. Two copper blocks) in contact attain thermal equilibrium when the heat transfer between them stops.

The equality of temperature is the only requirement for thermal equilibrium.

The Zeroth Law of Thermodynamics

If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.

This obvious fact cannot be concluded from the other laws of thermodynamics, and it serves as a basis of temperature measurement.

By replacing the third body with a thermometer, the zeroth law can be restated *two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact*

The zeroth law was first formulated and labeled by R.H. Fowler in 1931.

Temperature Scales

All temperature scales are based on some easily reproducible states such as the freezing and boiling point of water, which are also called the ice-point and the steam-point respectively.

A mixture of ice and water that is in equilibrium with air saturated with water vapour at 1atm pressure is said to be at the ice-point, and a mixture of liquid water and water vapour (with no air) in equilibrium at 1atm is said to be at the steam-point.

Celsius and Fahrenheit scales are based on these two points (although the value assigned to these two values is different) and are referred as two-point scales.

In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of the substance or substances.

Such a temperature scale is called a thermodynamic temperature scale.(Kelvin in SI)

Ideal gas temperature scale

The temperatures on this scale are measured using a constant volume thermometer.

Based on the principle that at low pressure, the temperature of the gas is proportional to its pressure at constant volume.

The relationship between the temperature and pressure of the gas in the vessel can be expressed as $T = a + b.P$

Where the values of the constants a and b for a gas thermometer are determined experimentally.

Once a and b are known, the temperature of a medium can be calculated from the relation above by immersing the rigid vessel of the gas thermometer into the medium and measuring the gas pressure.

Ideal gas temperature scale can be developed by measuring the pressures of the gas in the vessel at two reproducible points (such as the ice and steam points) and assigning suitable values to temperatures those two points.

Considering that only one straight line passes through two fixed points on a plane, these two measurements are sufficient to determine the constants a and b in the above equation.

If the ice and the steam points are assigned the values 0 and 100 respectively, then the gas temperature scale will be identical to the Celsius scale.

In this case, the value of the constant a (that corresponds to an absolute pressure of zero) is determined to be -273.15°C when extrapolated.

The equation reduces to $T = bP$, and thus we need to specify the temperature at only one point to define an absolute gas temperature scale.

Absolute gas temperature is identical to thermodynamic temperature in the temperature range in which the gas thermometer can be used.

We can view that thermodynamic temperature scale at this point as an absolute gas temperature scale that utilizes an ideal gas that always acts as a low-pressure gas regardless of the temperature.

At the Tenth international conference on weights and measures in 1954, the Celsius scale has been redefined in terms of a single fixed point and the absolute temperature scale.

The triple point occurs at a fixed temperature and pressure for a specified substance.

The selected single point is the triple point of water (the state in which all three phases of water coexist in equilibrium), which is assigned the value 0.01 C. As before the boiling point of water at 1 atm. Pressure is 100.0 C. Thus the new Celsius scale is essentially the same as the old one.

On the Kelvin scale, the size of Kelvin unit is defined as “ the fraction of $1/273.16$ of the thermodynamic temperature of the triple point of water, which is assigned a value of 273.16K ”. The ice point on Celsius and Kelvin are respectively 0 and 273.15 K.

GRAPHICAL REPRESENTATION OF DATA

1. Pressure versus temperature (P-T)
2. Pressure vs. volume (P-v)
3. Temperature vs. volume (T-v)
4. Temperature vs. entropy (T-s)
5. Enthalpy vs. entropy (h-s)
6. Pressure vs. enthalpy (P-h)

First Law Analysis to Non-flow Processes

Constant Volume process:

1. Heating of gas enclosed in a rigid vessel:

$$dU = dQ \text{ or } U_2 - U_1, Q = m C_v (T_2 - T_1)$$

2. Shaft work done on a system at constant volume

$$dU = dQ - dW = dQ - (dW_{pdv} + dW_s)$$

$$\text{or } dU = -dW_s \text{ or } -W_s = U_2 - U_1$$

3. Constant volume process involving electrical work:

$$-W_s = U_2 - U_1$$

For an adiabatic process the work is done is independent of path.

Constant Pressure Process

1. Reversible heating of a gas
2. Phase Change at constant pressure(Rev.)
3. Shaft work at constant pressure
4. Electrical work at constant pressure

$$W = P (V_2 - V_1)$$

$$dU = dQ - dW = dQ - PdV = dQ - d(PV)$$

$$\text{or, } dQ = dU + d(PV) = d(U + PV) = dH$$

$Q = \Delta H$ the heat interaction is equal to increase in enthalpy

Constant Temperature Process

$$dU = dQ - dW = dQ - PdV$$

for an ideal gas $u = u(T)$ then $dU = 0$

$$dQ = PdV = RT (dv/v)$$

$$Q = W = RT \ln (v_2/v_1)$$

Reversible Adiabatic Process

$$dU = -dW \text{ or } W = -\Delta U$$

This equation is true for reversible as well as irreversible process.

$$C_v dT = -PdV = -RT/v dv$$

$$dT/T = -R/C_v dv/v$$

$$R/C_v = \gamma - 1$$

$$dT/T = -(\gamma - 1) dv/v$$

$$T_2/T_1 = (v_1/v_2)^{(\gamma-1)} \quad T v^{(\gamma-1)} = \text{constant}$$

Also $P v^\gamma = \text{Constant}$ using perfect gas relation

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is the thermodynamic expression of the conservation of energy.

This law most simply stated by saying that “energy can not be created or destroyed” or that “the energy of the universe is constant”.

This law can be stated for a system (control mass) undergoing a cycle or for a change of state of a system.

Stated for a system undergoing a cycle, the cyclic integral of the work is proportional to the cyclic integral of the heat.

Mathematically stated, for a control mass undergoing a cyclic process such as in Joule's experiment and for consistent set of units

$$\int dQ_{\text{from system}} = \int dW_{\text{on system}}$$

$$\text{or } \int dQ_{\text{from system}} - \int dW_{\text{on system}} = 0$$

The important thing to remember is that the first law states that the energy is conserved always.

Sign convention The work done by a system on the surroundings is treated as a positive quantity.

Similarly, energy transfer as heat to the system from the surroundings is assigned a positive sign. With the sign convention one can write,

$$\int dQ = \int dW$$

Consequences of the first law: Suppose a system is taken from state 1 to state 2 by the path 1-a-2 and is restored to the initial state by the path 2-b-1, then the system has undergone a cyclic process 1-a-2-b-1. If the system is restored to the initial state by path 2-c-1, then the system has undergone the cyclic change 1-a-2-c-1. Let us apply the first law of thermodynamics to the cyclic processes 1-a-2-b-1 and 1-a-2-c-1 to obtain

$$\int_{1-a-2} dQ + \int_{2-b-1} dQ - \int_{1-a-2} dW - \int_{2-b-1} dW = 0$$

$$\int_{1-a-2} dQ + \int_{2-c-1} dQ - \int_{1-a-2} dW - \int_{2-c-1} dW = 0$$

Subtracting, we get

$$\int_{2b1} dQ - \int_{2c1} dQ - (\int_{2b1} dW - \int_{2c1} dW) = 0$$

We know that the work is a path function and hence the term in the bracket is non-zero. Hence we

$$\text{find } \int_{2b1} dQ = \int_{2c1} dQ$$

That is heat is also a path function.

Energy is a property of the system: By rearranging we can have

$$\int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW)$$

It shows that the integral is the same for the paths 2-b-1 and 2-c-1, connecting the states 2 and 1. That is, the quantity $\int (dQ - dW)$ does not depend on the path followed by a system, but depends only on the initial and the final states of the system. That is $\int (dQ - dW)$ is an exact differential of a property. This property is called energy (E). It is given by

$$dE = dQ - dW$$

$$E = KE + PE + U$$

where U is the internal energy. Therefore,

$$dE = d(KE) + d(PE) + dU = dQ - dW$$

Quit often in many situations the KE or PE changes are negligible.

$$dU = dQ - dW$$

An isolated system does not exchange energy with the surroundings in the form of work as well as heat. Hence $dQ = 0$ and $dW = 0$. Then the first law of thermodynamics reduces to $dE = 0$ or $E_2 = E_1$ that is energy of an isolated system remains constant.

Perpetual Motion Machine of the first kind: An imaginary device which delivers work continuously without absorbing energy from the surroundings is called a Perpetual Motion machine of the first kind. Since the device has to deliver work continuously, it has to operate on a cycle. If such a device does not absorb energy from its surroundings $\oint dQ = 0$. From the first law, it can be observed that $\oint dW = 0$, if $\oint dQ = 0$. Therefore such a device is impossible from first law of thermodynamics.

First law analysis of non-flow processes: The first law of thermodynamics can be applied to a system to evaluate the changes in its energy when it undergoes a change of state while interacting with its surroundings. The processes that are usually encountered in thermodynamic analysis of systems can be identified as any one or a combination of the following elementary processes:

- Constant volume (isochoric) process
- Constant pressure (isobaric) process
- Constant temperature (isothermal) process.
- Adiabatic process.

Constant volume process: Suppose a gas enclosed in a rigid vessel is interacting with the surroundings and absorbs energy Q as heat. Since the vessel is rigid, the work done W due to expansion or compression is zero. Applying the first law, we get

$$dU = dQ \text{ or } Q = U_2 - U_1$$

That is, heat interaction is equal to the change in internal energy of the gas. If the system contains a mass m equal of an ideal gas, then

$$Q = \Delta U = mC_v (T_2 - T_1)$$

The path followed by the gas is shown on a P-V diagram. Now consider the fluid contained in a rigid vessel as shown. The vessel is rigid and insulated. Shaft work is done on the system by a paddle wheel as shown in Fig. a. In Fig. b electric work is done on the system. Since the vessel is rigid, the PdV work is zero. Moreover, the vessel is insulated and hence $dQ = 0$. Application of the first law of thermodynamics gives

$$dU = dQ - dW = dQ - (dW_{pdv} + dW_s)$$

$$\text{or } dU = -dW_s \text{ or } -W_s = \Delta U = U_2 - U_1$$

Where dW_{pdv} is the compression /expansion work and dW_s is the shaft work. That is increase in internal energy of a system at a constant volume, which is enclosed by an adiabatic wall, is equal to the shaft work done on the system.

Constant pressure process: Several industrial processes are carried out at constant pressure. A few examples of constant pressure processes are: (a) reversible heating/cooling of a gas (b) phase change (c) paddle wheel work (d) electrical work. For a constant pressure process, the work done W is given by

$$W = \int PdV = P (V_2 - V_1)$$

Application of the first law of thermodynamics gives

$$dU = dQ - dW = dQ - PdV = dQ - d(PV)$$

$$\text{or } dQ = dU + d(PV) = d(U + PV) = dH$$

$$\text{or } Q = \Delta H$$

That is in a constant pressure process, the heat interaction is equal to the increase in the enthalpy of the system. Now consider the constant pressure processes in which the system is enclosed by an adiabatic boundary. Application of the first law gives:

$$dU = dQ - dW = dQ - (PdV + dW_s)$$

Here, the net work done (dW) consists of two parts – the PdV work associated with the motion of the boundary and ($-dW_s$), the shaft work (or electrical work) done by the surroundings. Since the system is enclosed by an adiabatic boundary, $dQ = 0$ the equation can be written as

$$-dW_s = dU + d(PV) = dH$$

That is, the increase in the enthalpy of the system is equal to the shaft work done on the system.

Constant temperature process: Suppose a gas enclosed in the piston cylinder assembly is allowed to expand from P_1 to P_2 while the temperature is held constant. Then application of the first law gives:

$$dU = dQ - dW = dQ - PdV$$

It is not possible to calculate work and heat interactions unless the relationships between the thermodynamic properties of the gas are known. Suppose the gas under consideration is an ideal gas (which follows the relation $Pv = RT$ and $u = u(T)$ only) then for an isothermal process,

$$dU = 0 \text{ and } dQ = PdV = RTdv/v \text{ or } Q = W = RT \ln(v_2/v_1)$$

Reversible adiabatic (Isentropic process):

Polytropic Process

$$W = \int cdv / v^n$$

$$w = (P_1 v_1 - P_2 v_2) / (n-1)$$

$$du = dq - dw$$

$$u_2 - u_1 = q - (P_1 v_1 - P_2 v_2) / (n-1)$$

$$u_2 - u_1 = C_v (T_2 - T_1) = q - w$$

$$q = R(T_2 - T_1) / (\gamma - 1) + (P_1 v_1 - P_2 v_2) / (n-1)$$

$$= R (T_1 - T_2) \{ 1/(n-1) - 1/(\gamma-1) \}$$

$$=(P_1 v_1 - P_2 v_2)/(n-1) \{(\gamma - n)/(\gamma - 1)\}$$

$$=w \cdot \{(\gamma - n)/(\gamma - 1)\}$$

Problem: Air (ideal gas with $\gamma = 1.4$) at 1 bar and 300K is compressed till the final volume is one-sixteenth of the original volume, following a polytropic process $Pv^{1.25} = \text{const}$. Calculate (a) the final pressure and temperature of the air, (b) the work done and (c) the energy transferred as heat per mole of the air.

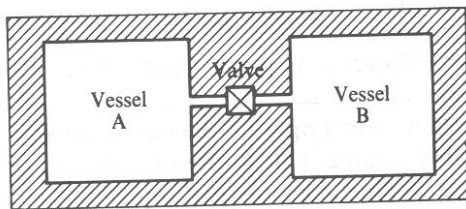
Solution: (a) $P_1 v_1^{1.25} = P_2 v_2^{1.25}$

$$P_2 = P_1 (v_1/v_2)^{1.25} = 1(16)^{1.25} = 32 \text{ bar}$$

$$T_2 = (T_1 P_2 v_2)/(P_1 v_1) = (300 \times 32 \times 1)/(1 \times 16) = 600\text{K}$$

$$\begin{aligned} \text{(b) } w &= (P_1 v_1 - P_2 v_2)/(n-1) \\ &= R_u (T_1 - T_2)/(n-1) \\ &= 8.314 (300 - 600)/(1.25-1) = -9.977 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \text{(c) } q &= w \cdot \{(\gamma - n)/(\gamma - 1)\} \\ &= -9.977 (1.4 - 1.25)/(1.4-1) \\ &= -3.742 \text{ kJ/mol} \end{aligned}$$



Unresisted or Free expansion

In an irreversible process, $w \neq \int P dv$

Vessel A: Filled with fluid at pressure

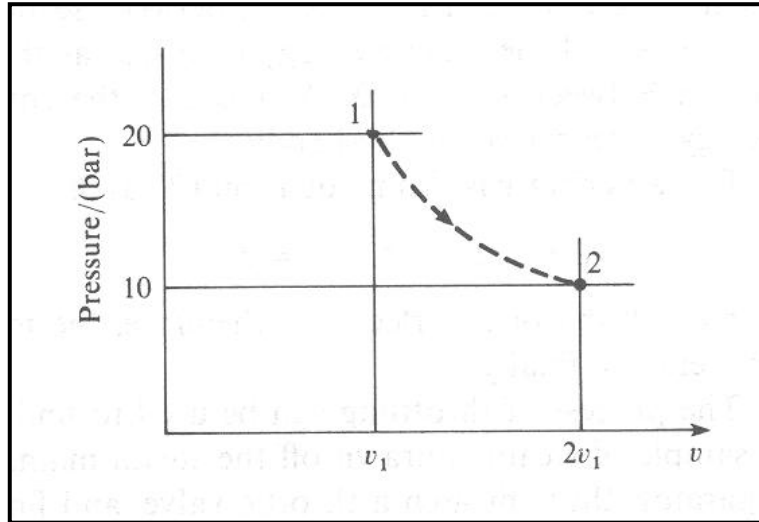
Vessel B: Evacuated/low pressure fluid

Valve is opened: Fluid in A expands and fills both vessels A and B. This is known as unresisted expansion or free expansion.

No work is done on or by the fluid.

No heat flows (Joule's experiment) from the boundaries as they are insulated.

$$U_2 = U_1 \quad (U = U_A + U_B)$$



Problem: A rigid and insulated container of 2m^3 capacity is divided into two equal compartments by a membrane. One compartment contains helium at 200kPa and 127°C while the second compartment contains nitrogen at 400kPa and 227°C . The membrane is punctured and the gases are allowed to mix. Determine the temperature and pressure after equilibrium has been established. Consider helium and nitrogen as perfect gases with their C_v as $3R/2$ and $5R/2$ respectively.

Solution: Considering the gases contained in both the compartments as the system, $W = 0$ and $Q = 0$. Therefore, $\Delta U = 0$ ($U_2 = U_1$)

$$\begin{aligned}\text{Amount of helium} &= N_{\text{He}} = P_A V_A / R_u T_A \\ &= 200 \times 10^3 \times 1 / (8.314 \times 400) \\ &= 60.14 \text{ mol.}\end{aligned}$$

$$\begin{aligned}\text{Amount of nitrogen} &= N_{\text{N}_2} = P_B V_B / R_u T_B \\ &= 400 \times 10^3 \times 1 / (8.314 \times 500) \\ &= 96.22 \text{ mol.}\end{aligned}$$

Let T_f be the final temperature after equilibrium has been established. Then,

$$[N C_v (T_f - 400)]_{\text{He}} + [N C_v (T_f - 500)]_{\text{N}_2} = 0$$

$$R_u [60.14 (T_f - 400) 3 + 96.22 (T_f - 500) 5] / 2 = 0$$

$$\text{Or, } T_f = 472.73 \text{ K}$$

The final pressure of the mixture can be obtained by applying the equation of state:

$$P_f V_f = (N_{\text{He}} + N_{\text{N}_2}) R_u T_f$$

$$2P_f = (60.14 + 96.22) 8.314 (472.73)$$

$$\text{or, } P_f = 307.27 \text{ kPa}$$

Control-Volume Analysis

Control volume is a volume in space of special interest for particular analysis.

The surface of the control volume is referred as a control surface and is a closed surface.
The surface is defined with relative to a coordinate system that may be fixed, moving or rotating.

Mass, heat and work can cross the control surface and mass and properties can change with time within the control volume.

Examples: turbines, compressors, nozzle, diffuser, pumps, heat exchanger, reactors, a thrust-producing device, and combinations of these.

First law of thermodynamics for a continuous system

Let the continuous system be in state 1 at time t and after a differential time dt , let it be in the state 2. The change in the energy of the continuous system is,

Now,
 $dE = dQ - dW$
or,

$$dE = \frac{d[\int \rho e dV]}{dt} dt$$

$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$
$$\frac{d}{dt} \int_V \rho e dV = \dot{Q} - \dot{W}$$

First law of thermodynamics to a control volume

$$\frac{dm}{dt} = \dot{m}_i - \dot{m}_e$$

Or

[Rate of accumulation of mass inside the control volume] = [Rate of mass entering the control volume at inlet] – [Rate of mass leaving the control volume at exit]

The above is commonly known as continuity equation.

We should identify a definite quantity of matter which remains constant as the matter flows. For this purpose, let the boundary of the system include all matter inside the control volume and that which is about to enter the control volume during the differential time interval dt .

At time t , the system is defined as the mass contained in the control volume and the mass in region A which is about to enter the control volume in a differential time dt .

At time $t+dt$, the system is defined as the mass contained in the control volume and the mass in region B.

Therefore, during the differential time dt , the system configuration undergoes a change.

Mass contained in region A = $\dot{m}_i dt$

Mass contained in region B = $\dot{m}_e dt$

From mass balance,

The work done as the $m(t) + \dot{m}_i dt = m(t+dt) + \dot{m}_e dt$ mass enters the control volume = $-P_i v_i \dot{m}_i dt$

The work done by mass exiting the control volume =

$P_e v_e \dot{m}_e dt$

Energy of the system at time $t = E(t) + \dot{m}_i e_i dt$

Energy of the system at time $(t+dt) =$

$E(t+dt) + e_e \dot{m}_e dt$

Energy transferred as heat to the system = $\dot{Q} dt$

Shaft work done by the system = $\dot{W}_{sh} dt$

From the first law,

$[E(t+dt) + e_e \dot{m}_e dt] - [E(t) + \dot{m}_i e_i dt] = \dot{Q} dt - \dot{W}_{sh} dt - (P_e v_e \dot{m}_e - P_i v_i \dot{m}_i) dt$

$\dot{m}_e (e_e + P_e v_e) - \dot{m}_i (e_i + P_i v_i) = \dot{Q} - \dot{W}_{sh} - \frac{E(t+dt) - E(t)}{dt}$

or,

$\dot{m}_e (h_e + V_e^2/2 + gZ_e) - \dot{m}_i (h_i + V_i^2/2 + gZ_i) = \dot{Q} - \dot{W}_{sh} - dE/dt$
 where, $h_e = u_e + P_e v_e$, $h_i = u_i + P_i v_i$

Or, Rate of energy accumulation = rate of energy inflow – rate of energy outflow

Steady state flow process

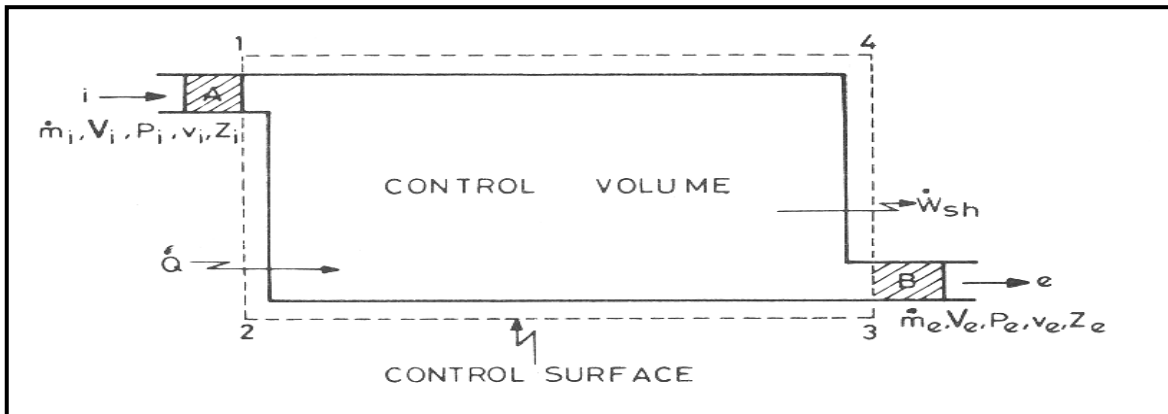
Assumptions:

$\dot{m}_i = \dot{m}_e = \dot{m}$
 The state of matter at the inlet, exit and at any given point inside the control volume does not change with respect to time.

$$dE / dt = 0$$

The rate of energy transfers across the control surface is constant.

$$(h_e + V_e^2/2 + gZ_e) - (h_i + V_i^2/2 + gZ_i) = (\dot{Q} - \dot{W}_{sh}) / \dot{m}$$



Steady state steady flow process

$$q - w = \Delta h + \Delta Ke + \Delta Pe = h_e - h_i + \frac{V_e^2 - V_i^2}{2} + g(Z_e - Z_i)$$

$$\text{where, } q = \dot{Q} / \dot{m} \text{ and } w = \dot{W}_{sh} / \dot{m}$$

For negligible change in kinetic and potential energies through the control volume,

$$q - w = \Delta h \quad (kJ / kg)$$

If the control volume is well insulated (i.e. adiabatic), then, $q = 0$.

For steady flow devices, such as turbines, compressors and pumps, \dot{W}_{sh} is power transmitted through a shaft.

$$\Delta Ke = (V_e^2 - V_i^2) / 2$$

The unit of ke is m^2/s^2 which is equivalent to Joule/kg. The enthalpy is usually given in kJ/kg. So kinetic energy should be expressed in kJ/kg. This is accomplished by dividing it by 1000.

Kinetic energy term at low velocities is negligible, but should be accounted for at high velocities.

By similar argument, the elevation difference between inlet and exit of most industrial devices such as compressors and turbines is small and potential energy term is negligible (particularly for gases). The only time the potential energy term is significant is when a process involves pumping a fluid to high elevations.

Turbine

A turbine is a rotary steady state steady flow machine whose purpose is the production of shaft power at the expense of the pressure of the working fluid.

Two general classes of turbines are steam and gas turbines depending on the working substance used.

Usually, changes in potential energy are negligible, as is the inlet kinetic energy. Often the exit kinetic energy is neglected (if in a problem, the flow velocities are specified, the kinetic energy term should be included).

Normally, the process in the turbine is adiabatic and the work output reduces to decrease in enthalpy from the inlet to exit states.

$$\dot{W}_{sh} = \dot{m}(h_i - h_e)$$

Compressor / pump

The purpose of a compressor (gas) or pump (liquid) is the same, to increase the pressure of a fluid by putting in shaft work (power). There are two fundamentally different types of compressors:

1. The rotary type (either axial or centrifugal flow)
2. A piston/cylinder type compressor.

The first type is analyzed using control volume approach (steady state steady flow process). The working fluid enters the compressor at low pressure and exits at high pressure.

Usually, changes in potential energy are negligible as is the inlet kinetic energy. Often, exit kinetic energy is neglected as well (wherever, in a problem, velocities are specified, *ke* term should not be neglected).

The compression process is usually adiabatic.

$$\dot{W}_{sh} = \dot{m}[(h_i - h_e) + (V_i^2 - V_e^2) / 2]$$

Nozzle

A nozzle is a steady state steady flow device to create a high velocity fluid stream at the expense of its pressure. It is contoured in an appropriate manner to expand the fluid to a lower pressure.

Since the objective of the device is to increase the flow velocity, hence kinetic energy, the kinetic energy term cannot be ignored. Usually, the process through the nozzle is treated as adiabatic.

Since there are no moving parts, shaft work is zero. The potential energy term (for gases) is negligible and hence omitted.

$$(h_i - h_e) = (V_e^2 - V_i^2) / 2$$

Diffuser

A steady state steady flow device meant to decelerate high velocity fluid resulting in increased pressure of the fluid. It is the opposite of a nozzle as far as the purpose is concerned. The assumptions are similar to those for a nozzle.

UNIT II

LIMITATIONS OF FIRST LAW

First law is a statement of conservation of energy principle. Satisfaction of first law alone does not ensure that the process will actually take place.

Examples:

1. A cup of hot coffee left in a cooler room eventually cools off. The reverse of this process- coffee getting hotter as a result of heat transfer from a cooler room does not take place.
2. Consider heating of a room by passage of electric current through an electric resistor. Transferring of heat from room will not cause electrical energy to be generated through the wire.
3. Consider a paddle-wheel mechanism operated by fall of mass. Potential energy of mass decreases and internal energy of the fluid increases. Reverse process does not happen, although this would not violate first law.
4. Water flows down hill where by potential energy is converted into K.E. Reverse of this process does not occur in nature.

Conclusion:

Processes proceed in a certain direction and not in the reverse direction. The first law places no restriction on direction.

A process will not occur unless it satisfies both the first and second laws of thermodynamics.

Second law not only identifies the direction of process, it also asserts that energy has quality as well as quantity.

Thermal Reservoir

A thermal reservoir is a large system (very high mass \times specific heat value) from which a quantity of energy can be absorbed or added as heat without changing its temperature. The atmosphere and sea are examples of thermal reservoirs.

Any physical body whose thermal energy capacity is large relative to the amount of energy it supplies or absorbs can be modeled as a thermal reservoir.

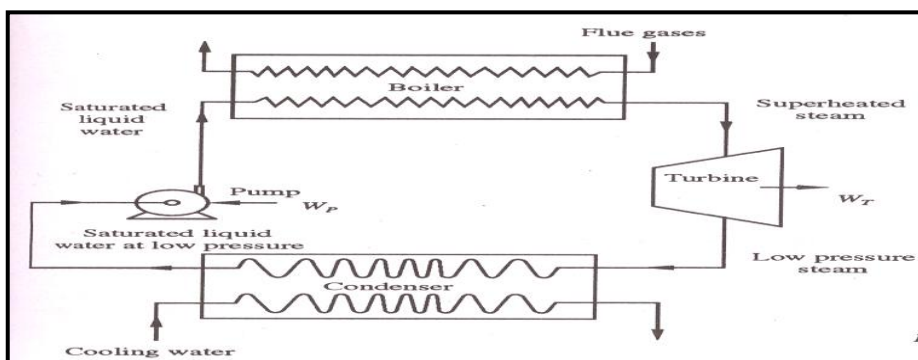
A reservoir that supplies energy in the form of heat is called a source and one that absorbs energy in the form of heat is called a sink.

Heat Engine

It is a cyclically operating device which absorbs energy as heat from a high temperature reservoir, converts part of the energy into work and rejects the rest of the energy as heat to a thermal reservoir at low temperature.

The working fluid is a substance, which absorbs energy as heat from a source, and rejects energy as heat to a sink.

Thermal Power Plant



Working Fluid ----- Water

Q_1 – Heat received from hot gases

W_T – Shaft work by turbine

Q_2 – Heat rejected to cooling water in condenser

W_P – Work done on the pump

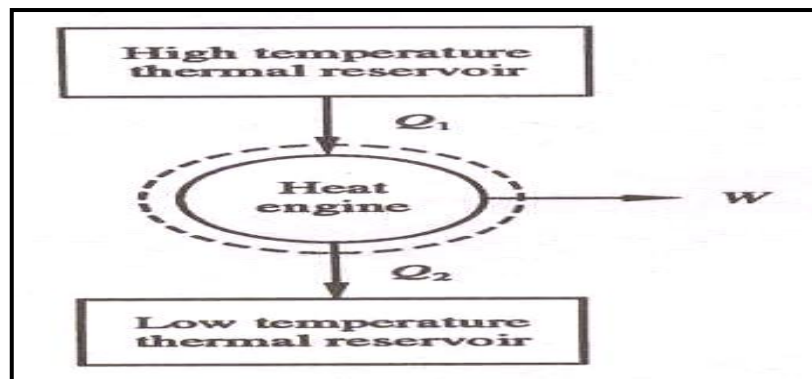
$$W_{net} = W_T - W_P$$

$$W = Q_1 - Q_2$$

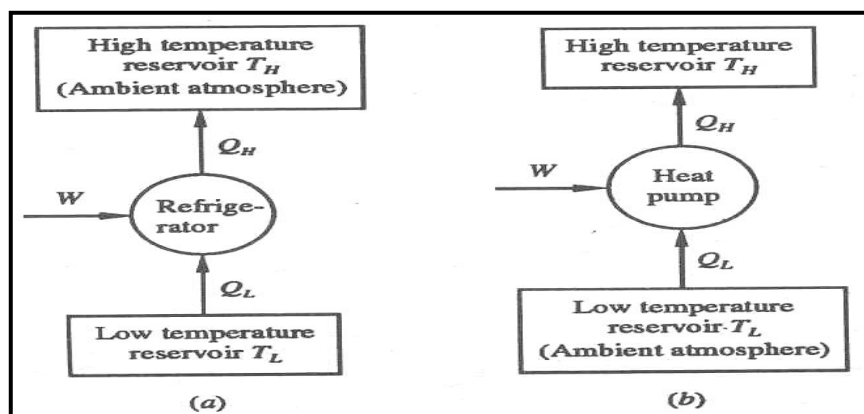
Thermal Efficiency,

$$\eta = \frac{W_{net}}{Q_1} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Schematic representation of Heat Engine



Schematic representation of Refrigerator and Heat pump.



Q_L – Heat absorbed from low temperature thermal reservoir

Q_H – Heat rejected to a high temperature thermal reservoir when work (W) is done on it.

$$(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$(COP)_{HP} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}$$

In a reversible, isothermal expansion of an ideal gas, all the energy absorbed as heat by the system is converted completely into work. However this cannot produce work continuously (not a cycle).

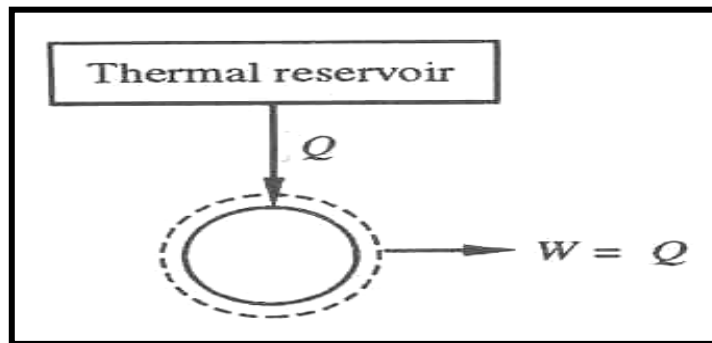
Single reservoir heat engine (1 T engine) is not possible.

Second Law of Thermodynamics

Kelvin-Planck Statement: - It is impossible to devise a cyclically operating device, which produces no other effect than the extraction of heat from a single thermal reservoir and delivers an equivalent amount of work.

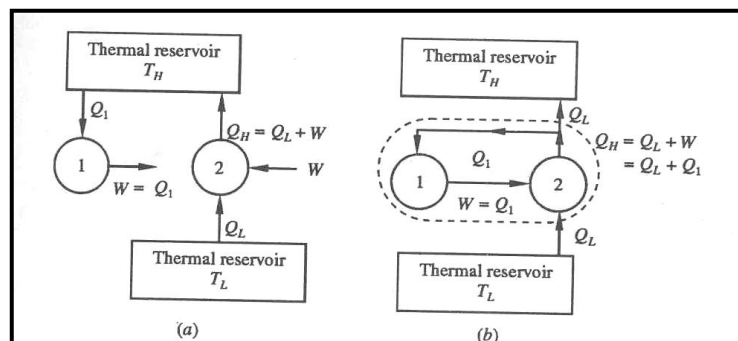
Heat engine with single thermal reservoir is not possible.

For a 1-T engine the thermal efficiency $\eta = W/Q = 1$. No heat engine can have efficiency equal to unity.



Clausius Statement: - It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body.

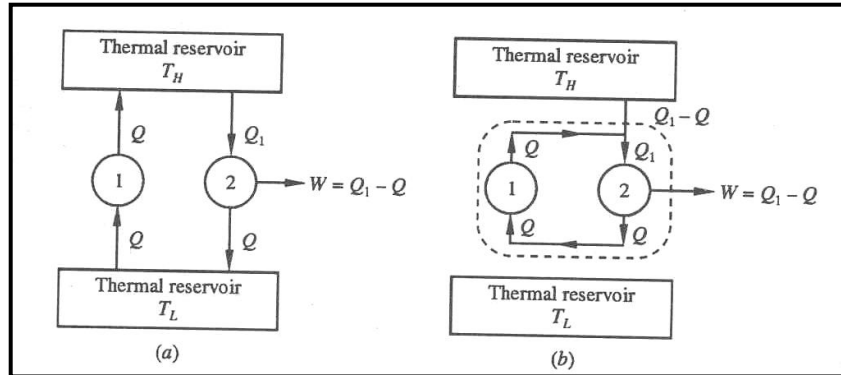
Equivalence of the two statements



To prove that violation of the Kelvin-Planck Statement leads to a violation of the Clausius Statement, let us assume that Kelvin-Planck statement is incorrect.

Consider a cyclically working device 1, which absorbs energy Q_1 as heat from a thermal reservoir at T_H . Equivalent amount of work $W(W=Q_1)$ is performed.

Consider another device 2 operating as a cycle, which absorbs energy Q_L as heat from a low



temperature thermal reservoir at T_L and rejects energy Q_H ($Q_H=Q_L+W$). Such a device does not violate Clausius statement.

If the two devices are now combined, the combined device (enclosed by the dotted boundary) transfers heat Q_L from the low temperature reservoir at T_L to a high temperature reservoir at T_H with out receiving any aid from an external agent, which is the violation of the Clausius statement.

Likewise let us assume that the Clausius statement is incorrect. So we have a device 1, cyclically working transferring heat Q from a low temperature reservoir at T_L to a high temperature thermal reservoir at T_H . Consider another device 2, which absorbs heat Q_1 from a high temperature reservoir at T_H does work W and rejects energy Q as heat tot the low temperature reservoir at T_L as shown in figure.

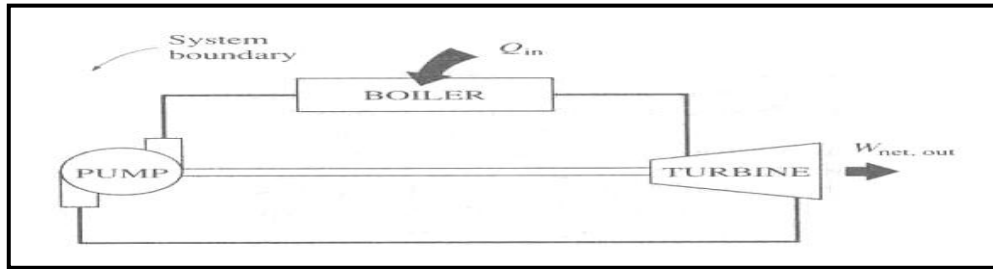
If the two devices are combined (shown in figure by a dotted enclosure), then the combined device receives energy (Q_1-Q) as heat from a thermal reservoir and delivers equivalent work ($W=Q_1-Q$) in violation of the Kelvin-Planck statement.

Therefore violation of Clausius statement leads to the violation of the Kelvin-Planck statement. Hence, these two statements are equivalent.

Perpetual Motion Machines

A device that violates the First law of thermodynamics (by creating energy) is called a Perpetual Motion Machine of the first kind.

A device that violates the Second law of thermodynamics is called a Perpetual Motion Machine of the Second kind.



The first device supplies continuously energy with out receiving it. So this is a system creating energy and therefore violating the first law.

The second device exchanges heat with a single reservoir and thus a net amount of work. This need not violate the first law, but violates the second law and therefore will not work.

Reversible and Irreversible Processes

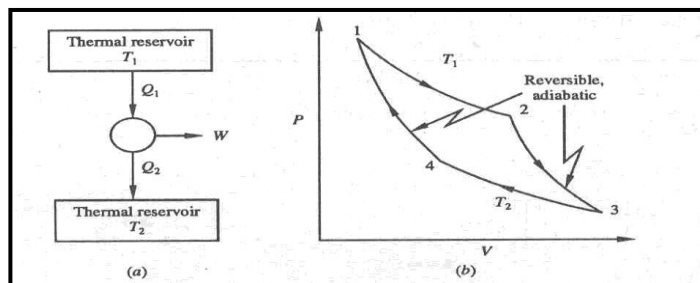
A process is said to be reversible if both the system and the surroundings can be restored to their respective initial states, by reversing the direction of the process. A reversible process is a process that can be reversed without leaving a trace on the surroundings. Processes that are not reversible are called Irreversible processes.

Irreversibilities

The factors that cause a process to be irreversible are called irreversibilities. Examples:

1. Friction
2. Unrestrained expansion
3. Mixing of two gases
4. Heat transfer across a finite temperature difference
5. Spontaneous chemical reactions
6. Expansion or Compression with finite pressure difference
7. Mixing of matter at different states

Carnot Cycle



The Carnot cycle uses only two thermal reservoirs – one at high temperature T_1 and the other at two temperature T_2 .

If the process undergone by the working fluid during the cycle is to be reversible, the heat transfer must take place with no temperature difference, i.e. it should be isothermal.

The Carnot cycle consists of a reversible isothermal expansion from state 1 to 2, reversible adiabatic expansion from state 2 to 3, a reversible isothermal compression from state 3 to 4 followed by a reversible adiabatic compression to state 1.

The thermal efficiency, η is given by

$\eta = \text{Net work done} / \text{Energy absorbed as heat}$

During processes 2-3 and 4-1, there is no heat interaction as they are adiabatic.

$$Q_{1-2} = \int_1^2 P dv = \int_1^2 RT_1 \frac{dv}{v} = RT_1 \ln(v_2 / v_1)$$

Similarly for the process 3-4,

$$Q_{3-4} = \int_3^4 P dv = \int_3^4 RT_2 \frac{dv}{v} = RT_2 \ln(v_4 / v_3)$$

Net heat interaction = Net work done

$$= RT_1 \ln(v_2/v_1) + RT_2 \ln(v_4/v_3)$$

$$= RT_1 \ln(v_2/v_1) - RT_2 \ln(v_3/v_4)$$

The processes 2-3 and 4-1 are reversible, adiabatic and hence

$$T_1 v_2^{\gamma-1} = T_2 v_3^{\gamma-1}$$

$$\text{Or, } v_2/v_3 = (T_2/T_1)^{1/(\gamma-1)}$$

$$\text{And } T_2 v_4^{\gamma-1} = T_1 v_1^{\gamma-1}$$

$$\text{Or, } v_1/v_4 = (T_2/T_1)^{1/(\gamma-1)}$$

$$v_2/v_3 = v_1/v_4 \text{ or } v_2/v_1 = v_3/v_4$$

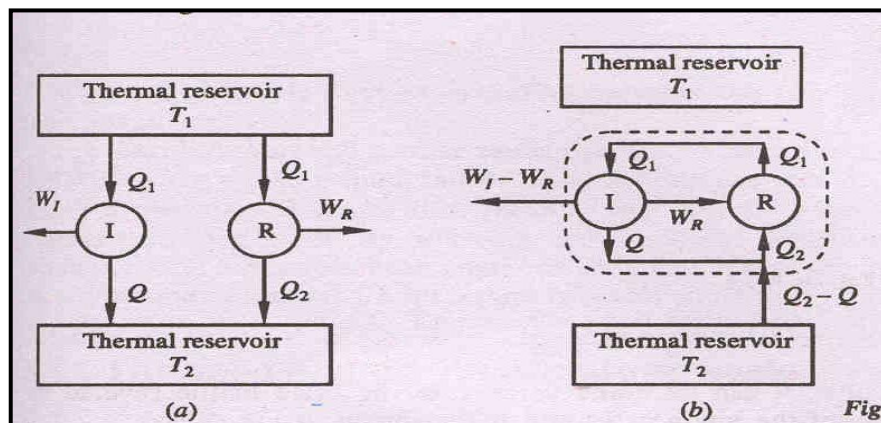
$$\eta = \{RT_1 \ln(v_2/v_1) - RT_2 \ln(v_3/v_4)\} / RT_1 \ln(v_2/v_1)$$

$$\eta = (T_1 - T_2)/T_1$$

$$= 1 - T_2/T_1$$

The Carnot Principles

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between same two thermal reservoirs.
2. The efficiencies of all reversible heat engines operating between the same two thermal reservoirs are the same.



Lets us assume it is possible for an engine I to have an efficiency greater than the efficiency of a reversible heat engine R.

$$\eta_I > \eta_R$$

Let both the engines absorb same quantity of energy Q_1 . Let Q and Q_2 represent the energy rejected as heat by the engines R, and I respectively.

$$W_I = Q_1 - Q$$

$$W_R = Q_1 - Q_2$$

$$\eta_I = W_I / Q_1 = (Q_1 - Q) / Q_1 = 1 - Q / Q_1$$

$$\eta_R = W_R / Q_1 = (Q_1 - Q_2) / Q_1 = 1 - Q_2 / Q_1$$

Since $\eta_I > \eta_R$,

$$1 - Q / Q_1 > 1 - Q_2 / Q_1$$

or, $Q < Q_2$

Therefore, $W_I (= Q_1 - Q) > W_R (= Q_1 - Q_2)$

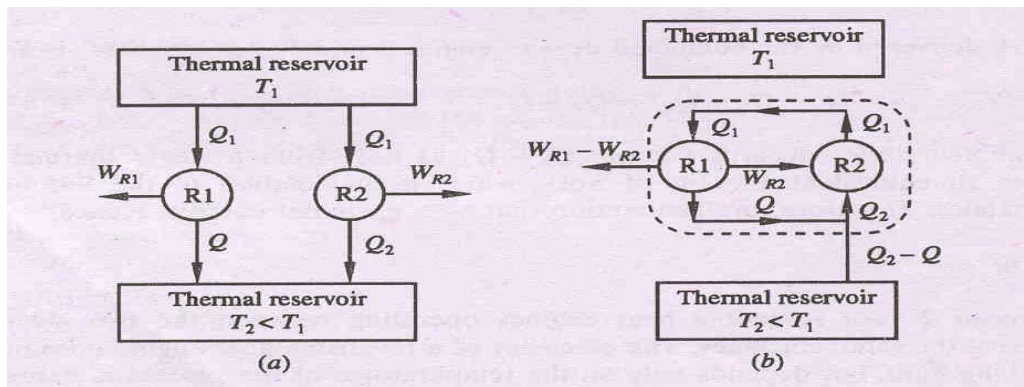
Since the engine R is reversible, it can be made to execute in the reverse order. Then, it will absorb energy Q_2 from the reservoir at T_2 and reject energy Q_1 to the reservoir at T_1 when work W_R is done on it.

If now engines I and R are combined, the net work delivered by the combined device is given by

$$W_I - W_R = Q_1 - Q - (Q_1 - Q_2) = Q_2 - Q$$

The combined device absorbs energy $(Q_2 - Q)$ as heat from a single thermal reservoir and delivers an equivalent amount of work, which violates the second law of thermodynamics.

Hence, $\eta_R \geq \eta_I$



Carnot principle 2

Consider two reversible heat engines R_1 and R_2 , operating between the two given thermal reservoirs at temperatures T_1 and T_2 .

Let $\eta_{R1} > \eta_{R2}$

Q_1 = energy absorbed as heat from the reservoir at T_1 by the engines R_1 and R_2 , separately.

Q = energy rejected by reversible engine R_1 to the reservoir at T_2

Q_2 = energy rejected by reversible engine R_2 to the reservoir at T_2 .

$W_{R1} = Q_1 - Q$ = work done by a reversible engine R_1 .

$W_{R2} = Q_1 - Q_2$ = work done by a reversible engine R_2

According to assumption,

$$\eta_{R1} > \eta_{R2}$$

$$\text{Or, } 1 - Q/Q_1 > 1 - Q_2/Q_1$$

$$Q_1 - Q > Q_1 - Q_2 \text{ or } W_{R1} > W_{R2}$$

$$W_{R1} - W_{R2} = (Q_1 - Q) - (Q_1 - Q_2) = Q_2 - Q$$

Since the engine R_2 is reversible, it can be made to execute the cycle in the reverse by supplying W_{R2} .

Since $W_{R1} > W_{R2}$ the reversible engine R_2 can be run as a heat pump by utilizing part of the work delivered by R_1 .

For the combined device,

$W_{R1} - W_{R2} = Q_2 - Q$, by absorbing energy $Q_2 - Q$ from a single thermal reservoir which violates the second law of thermodynamics.

Hence $\eta_{R1} > \eta_{R2}$ is incorrect.

By similar arguments, if we assume that $\eta_{R2} > \eta_{R1}$ then,

$$\eta_{R1} \geq \eta_{R2}$$

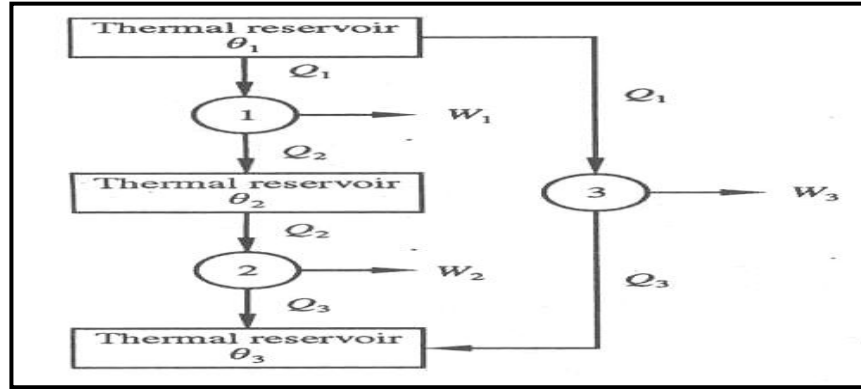
Therefore, based on these two equations,

$$\eta_{R1} = \eta_{R2}$$

The efficiency of a reversible heat engine is also independent of the working fluid and depends only on the temperatures of the reservoirs between which it operates.

Thermodynamic Temperature Scale

To define a temperature scale that does not depend on the thermometric property of a substance, Carnot principle can be used since the Carnot engine efficiency does not depend on the working fluid. It depends on the temperatures of the reservoirs between which it operates.



Consider the operation of three reversible engines 1, 2 and 3. The engine 1 absorbs energy Q_1 as heat from the reservoir at T_1 , does work W_1 and rejects energy Q_2 as heat to the reservoir at T_2 .

Let the engine 2 absorb energy Q_2 as heat from the reservoir at T_2 and does work W_2 and rejects energy Q_3 as heat to the reservoir at T_3 .

The third reversible engine 3, absorbs energy Q_1 as heat from the reservoir at T_1 , does work W_3 and rejects energy Q_3 as heat to the reservoir at T_3 .

$$\eta_1 = W_1 / Q_1 = 1 - Q_2/Q_1 = f(T_1, T_2)$$

$$\text{or, } Q_1/Q_2 = F(T_1, T_2)$$

$$\eta_2 = 1 - Q_3/Q_2 = f(T_2, T_3)$$

$$\text{or, } T_2/T_3 = F(T_2, T_3)$$

$$\eta_3 = 1 - Q_3/Q_1 = f(T_1, T_3)$$

$$T_1/T_3 = F(T_1, T_3)$$

$$\text{Then, } Q_1/Q_2 = (Q_1/Q_3)/(Q_2/Q_3)$$

$$\text{Or, } F(T_1, T_2) = F(T_1, T_3) / F(T_2, T_3)$$

Since T_3 does not appear on the left side, on the RHS also T_3 should cancel out. This is possible if the function F can be written as

$$F(T_1, T_2) = \phi(T_1) \psi(T_2)$$

$$\begin{aligned} \phi(T_1) \psi(T_2) &= \{\phi(T_1) \psi(T_3)\} / \{\phi(T_2) \psi(T_3)\} \\ &= \phi(T_1) \psi(T_2) \end{aligned}$$

$$\text{Therefore, } \psi(T_2) = 1 / \phi(T_2)$$

$$\text{Hence, } Q_1 / Q_2 = F(T_1, T_2) = \phi(T_1) / \phi(T_2)$$

Now, there are several functional relations that will satisfy this equation. For the thermodynamic scale of temperature, Kelvin selected the relation

$$Q_1/Q_2 = T_1/T_2$$

That is, the ratio of energy absorbed to the energy rejected as heat by a reversible engine is equal to the ratio of the temperatures of the source and the sink.

The equation can be used to determine the temperature of any reservoir by operating a reversible engine between that reservoir and another easily reproducible reservoir and by measuring efficiency (heat interactions). The temperature of easily reproducible thermal reservoir can be arbitrarily assigned a numerical value (the reproducible reservoir can be at triple point of water and the temperature value assigned 273.16 K).

The efficiency of a Carnot engine operating between two thermal reservoirs the temperatures of which are measured on the thermodynamic temperature scale, is given by

$$\eta_1 = 1 - Q_2/Q_1 = 1 - T_2/T_1$$

The efficiency of a Carnot engine, using an ideal gas as the working medium and the temperature measured on the ideal gas temperature scale is also given by a similar expression.

$$(\text{COP})_R = Q_L / (Q_H - Q_L) = T_L / (T_H - T_L)$$

$$(\text{COP})_{HP} = Q_H / (Q_H - Q_L) = T_H / (T_H - T_L)$$

Clausius Inequality

For a Carnot cycle

$$Q_1/Q_2 = T_1/T_2$$

Or $Q_1/T_1 - Q_2/T_2 = 0$ for a reversible engine.

With the usual sign convention, that is, heat flow into a system taken as positive and heat outflow of the system taken as negative

$$Q_1/T_1 + Q_2/T_2 = 0 \quad \text{or} \quad \sum Q_i/T_i = 0$$

For an irreversible engine absorbing Q_1 amount of heat from a reservoir at T_1 and rejecting Q_2^1 to a reservoir at T_2 , then

$$1 - Q_2^1/Q_1 < 1 - Q_2/Q_1$$

$$\text{or} \quad 1 - Q_2^1/Q_1 < 1 - T_2/T_1$$

$$\text{or} \quad Q_2^1/Q_1 > T_2/T_1$$

$$\text{or} \quad Q_2^1/T_2 > Q_1/T_1$$

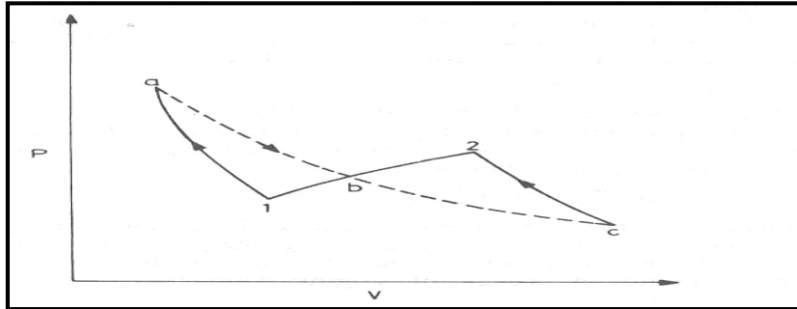
Making use of the sign convention, we get

$$Q_2^1/T_2 + Q_1/T_1 < 0$$

Or $\Sigma Q/T < 0$ for an irreversible engine

Replacement of a Reversible process by an equivalent process

Let us consider cyclic changes in a system other than heat engines. If the cycle can be split up into a large number of heat engine cycles then the above observation can be made use of in relating the heat interactions with the absolute temperatures.



Any reversible process can be approximated by a series of reversible, isothermal and reversible, adiabatic processes.

Consider a reversible process 1-2. The same change of a state can be achieved by process 1-a (reversible adiabatic process), isothermal process a-b-c and a reversible adiabatic process c-2. The areas 1-a-b and b-c-2 are equal. From the first law

$$U_2 - U_1 = Q_{1-a-b-c-2} - W_{1-a-b-c-2}$$

Consider the cycle 1-a-b-c-2-b-1. The net work of the cycle is zero. Then

$$\oint dW = W_{1-a-b-c-2} + W_{2-b-1} = 0$$

or

$$W_{1-a-b-c-2} = -W_{2-b-1} = W_{1-b-2}$$

The heat interaction along the path 1-a-b-c-2 is

$$Q_{1-a-b-c-2} = Q_{1-a} + Q_{a-b-c} + Q_{c-2} = Q_{a-b-c}$$

Since 1-a and c-2 are reversible adiabatic paths. Hence

$$U_2 - U_1 = Q_{a-b-c} - W_{1-b-2}$$

Application of the first law of the thermodynamics to the process 1-b-2 gives

$$U_2 - U_1 = Q_{1-b-2} - W_{1-b-2}$$

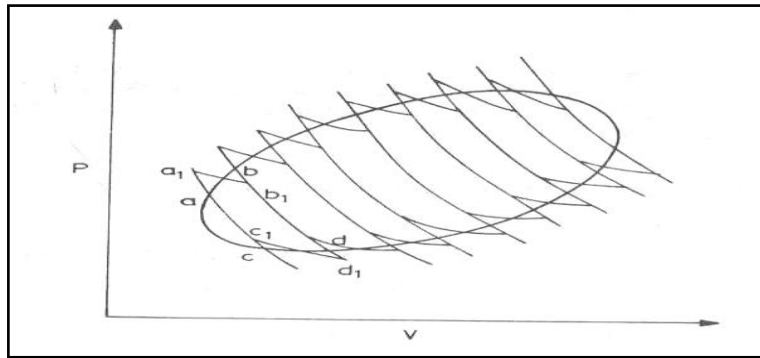
Comparing the two equations

$$Q_{i-b-c} = Q_{1-b-2}$$

The heat interaction along the reversible path 1-b-2 is equal to that along the isothermal path a-b-c. Therefore a reversible process can be replaced by a series of reversible adiabatic and reversible isothermal processes.

Clausius Inequality

A given cycle may be subdivided by drawing a family of reversible, adiabatic lines. Every two adjacent adiabatic lines may be joined by two reversible isotherms.



The heat interaction along the reversible path is equal to the heat interaction along the reversible isothermal path.

The work interaction along the reversible path is equal to the work interaction along the reversible adiabatic and the reversible isothermal path.

That is,

$$Q_{a-b} = Q_{a1-b1} \text{ and } Q_{c-d} = Q_{c1-d1}$$

a1-b1-d1-c1 is a Carnot cycle.

The original reversible cycle thus is a split into a family of Carnot cycles. For every Carnot cycle

$$\oint dQ / T = 0$$

. Therefore for the given reversible cycle,

$$\oint dQ / T = 0$$

If the original cycle is irreversible

$$\oint dQ/T < 0$$

so the generalized observation is

$$\oint dQ/T \leq 0$$

Whenever a system undergoes a cyclic change, however complex the cycle may be (as long as it involves heat and work interactions), the algebraic sum of all the heat interactions divided by the absolute temperature at which heat interactions are taking place considered over the entire cycle is less than or equal to zero (for a reversible cycle).

Entropy

1. $\int \frac{dQ}{T}$ has the same value irrespective of path as long as path is reversible

2. $\left(\frac{dQ}{T}\right)_R$ is an exact differential of some function which is identical as entropy

3. $S_2 - S_1 = \Delta S = \int_1^2 dS = \int_1^2 \left(\frac{dQ}{T}\right)_R$

4. $dS = \left(\frac{dQ}{T}\right)_R$ for reversible process only

Calculation of Entropy change

1. Entropy is a state function. The entropy change is determined by its initial and final states only
2. In analyzing irreversible process, it is not necessary to make a direct analysis of actual reversible process.

Substitute actual process by an imaginary reversible process. The entropy change for imaginary reversible process is same as that of an irreversible process between given final and initial states.

(a) Absorption of energy by a constant temperature reservoir

Energy can be added reversibly or irreversibly as heat or by performing work.

$$\Delta S = \int \left(\frac{dQ}{T}\right)_R$$

Example:-

The contents of a large constant-temperature reservoir maintained at 500 K are continuously stirred by a paddle wheel driven by an electric motor. Estimate the entropy change of the reservoir if the paddle wheel is operated for two hours by a 250W motor.

Paddle wheel work converted into internal energy- an irreversible process. Imagine a reversible process with identical energy addition

$$\Delta S = \int \left(\frac{dQ}{T} \right)_R = \frac{Q}{T} = \frac{0.25 \times 2(3600)}{500} = 0.6 kJ$$

(b) Heating or cooling of matter

$$Q = \Delta U \quad \text{for constant volume heating}$$

$$Q = \Delta H \quad \text{for constant pressure heating}$$

$$\Delta S = \int \frac{dQ}{T} = m \int_{T_1}^{T_2} C_p \frac{dT}{T} = m C_p \ln \left(\frac{T_2}{T_1} \right)$$

for constant pressure

$$\Delta S = \int \frac{dQ}{T} = m \int_{T_1}^{T_2} C_v \frac{dT}{T} = m C_v \ln \left(\frac{T_2}{T_1} \right)$$

, for constant volume process

Example: -

Calculate entropy change if 1kg of water at 30°C is heated to 80°C at 1 bar pressure. The specific heat of water is 4.2kJ/kg-K

$$\begin{aligned} \Delta S &= C_p \ln \left(\frac{T_2}{T_1} \right) = 4.2 \times 10^3 \times \ln \left(\frac{273+80}{273+30} \right) \\ &= 0.6415 \frac{kJ}{kg.K} \end{aligned}$$

(c) Phase change at constant temperature and pressure

$$S_{sf} = \int \frac{dQ}{T} = \frac{h_{sf}}{T_{sf}}$$

$$S_{fg} = \int \frac{dQ}{T} = \frac{h_{fg}}{T}$$

Example:-

Ice melts at 0°C with latent heat of fusion = 339.92 kJ/kg. Water boils at atmospheric pressure at 100°C with $h_{fg} = 2257$ kJ/kg.

$$S_{sf} = \frac{334.92}{273.15} = 1.2261 \frac{\text{kJ}}{\text{kg.K}}$$

$$S_{fg} = \frac{2257}{373.15} = 6.0485 \frac{\text{kJ}}{\text{kg.K}}$$

(d) Adiabatic mixing**Example:-**

A lump of steel of mass 30kg at 427°C is dropped in 100kg oil at 27°C . The specific heats of steel and oil is 0.5kJ/kg-K and 3.0 kJ/kg-K respectively. Calculate entropy change of steel, oil and universe.

T = final equilibrium temperature.

$$(mC_p \Delta T)_{\text{steel}} = (mC_p \Delta T)_{\text{oil}}$$

$$300 \times 0.5 \times (700 - T) = 100 \times 3 \times (T - 300)$$

or T = 319K

$$\begin{aligned} (\Delta S)_{\text{steel}} &= \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{mC_p dT}{T} = \left(mC_p \ln \frac{T_2}{T_1} \right)_{\text{steel}} \\ &= 30 \times 0.5 \times \ln \left(\frac{319}{700} \right) = -11.7883 \text{ kJ / K} \end{aligned}$$

$$\begin{aligned} (\Delta S)_{\text{oil}} &= \left(mC_p \ln \frac{T_2}{T_1} \right)_{\text{oil}} \\ &= 100 \times 3 \times \ln \left(\frac{319}{300} \right) = 18.4226 \text{ kJ / K} \end{aligned}$$

$$(\Delta S)_{\text{universe}} = -11.7883 + 18.4226 = 6.6343 \text{ kJ / K}$$

Tds relations

From the definition of entropy,

$$dQ = Tds$$

From the first law of thermodynamics,

$$dW = PdV$$

Therefore,

$$TdS = dU + PdV$$

$$\text{Or, } Tds = du + Pdv$$

This is known as the first Tds or, **Gibbs equation**.

The second Tds equation is obtained by eliminating du from the above equation using the definition of enthalpy.

$$h = u + Pv \rightarrow dh = du + vdP$$

$$\text{Therefore, } Tds = dh - vdP$$

The two equations can be rearranged as

$$ds = (du/T) + (Pdv/T)$$

$$ds = (dh/T) - (vdP/T)$$

Change of state for an ideal gas

If an ideal gas undergoes a change from P_1, v_1, T_1 to P_2, v_2, T_2 the change in entropy can be calculated by devising a reversible path connecting the two given states.

Let us consider two paths by which a gas can be taken from the initial state, 1 to the final state, 2.

The gas in state 1 is heated at constant pressure till the temperature T_2 is attained and then it is brought reversibly and isothermally to the final pressure P_2 .

Path 1-a: reversible, constant-pressure process.

Path a-2: reversible, isothermal path

$$\Delta s_{1-a} = \int dq/T = \int C_p dT/T = C_p \ln(T_2/T_1)$$

$$\Delta s_{a-2} = \int dq/T = \int (du + PdV)/T = \int (PdV)/T = R \ln(v_2/v_a)$$

(Since $du = 0$ for an isothermal process)

$$\text{Since } P_2 v_2 = P_a v_a = P_1 v_a$$

$$\text{Or, } v_2/v_a = P_1/P_2$$

$$\text{Or, } \Delta s_{a-2} = -R \ln(P_2/P_1)$$

Therefore, $\Delta s = \Delta s_{1-a} + \Delta s_{a-2}$

$$= C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

Path 1-b-2: The gas initially in state 1 is heated at constant volume to the final temperature T_2 and then it is reversibly and isothermally changed to the final pressure P_2 .

1-b: reversible, constant volume process

b-2: reversible, isothermal process

$$\Delta s_{1-b} = C_v \ln(T_2/T_1)$$

$$\Delta s_{b-2} = R \ln(v_2/v_1)$$

$$\text{or, } \Delta s = C_v \ln(T_2/T_1) + R \ln(v_2/v_1)$$

The above equation for Δs can also be deduced in the following manner:

$$ds = (dq/T)_R = (du + PdV)/T = (dh - v dP)/T$$

$$\begin{aligned} \text{or, } \Delta s &= \int_1^2 \frac{(du + p dV)}{T} = \int_1^2 \frac{C_v dT}{T} + \frac{R dV}{V} \\ &= C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \end{aligned}$$

Similarly,

$$\Delta s = \int_1^2 \frac{(dh - v dp)}{T} = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Principle of increase of entropy

Let a system change from state 1 to state 2 by a reversible process A and return to state 1 by another reversible process B. Then 1A2B1 is a reversible cycle. Therefore, the Clausius inequality gives:

$$\int_{1A2B1} dQ/T = \int_{1A2} dQ/T + \int_{2B1} dQ/t = 0$$

If the system is restored to the initial state from 1 to state 2 by an irreversible process C, then 1A2C1 is an irreversible cycle. Then the Clausius inequality gives:

$$\int_{1A2C1} dQ/T = \int_{1A2} dQ/T + \int_{2C1} dQ/t = 0$$

Subtracting the above equation from the first one,

$$\int_{2B1} dQ/T > \int_{2C1} dQ/T$$

Since the process 2B1 is reversible,

$$\int_{2B1} dQ/T = \int_1^2 dQ/T$$

Where the equality sign holds good for a reversible process and the inequality sign holds good for an irreversible process.

Now let us apply the above result to evaluate the entropy change of the universe when a system interacts with its surroundings and exchanges energy as heat with the surroundings.

Let T_{sur} and T_{sys} be the temperatures of the surroundings and the system such that $T_{\text{sur}} > T_{\text{sys}}$. Let dQ represent the energy transfer as heat from the surroundings to the system during the given irreversible process.

$$dS_{\text{sys}} = dQ/T_{\text{sys}}$$

$$dS_{\text{sur}} = -dQ/T_{\text{sur}}$$

$$dS_{\text{uni}} = dS_{\text{sys}} + dS_{\text{sur}} = (dQ/T)_{\text{sys}} - (dQ/T)_{\text{sur}} > 0$$

$$\Delta S_{\text{uni}} > 0 \text{ (since } T_{\text{sur}} > T_{\text{sys}} \text{)}$$

If the system is isolated, there is no change in the entropy of the surroundings and $\Delta S \geq 0$, for an isolated system

Therefore the entropy of an isolated system either increases or, in the limit, remains constant.

The equality sign holds good when the process undergone by the system is reversible, the inequality sign holds good if there is any irreversibility present in the process. This statement is usually called the **principle of entropy increase**.

Irreversible or spontaneous processes can occur only in that direction for which the entropy of the universe or that of an isolated system, increases. These processes cannot occur in the direction of decreasing entropy.

For an isolated system,

$$\Delta S > 0, \text{ for irreversible processes}$$

$$\Delta S = 0, \text{ for reversible processes}$$

$$\Delta S < 0, \text{ the process is impossible}$$

Example:

One kg of superheated steam at 0.2MPa and 200°C contained in a piston cylinder assembly is kept at ambient conditions of 300K till the steam is condensed to saturated liquid at constant pressure. Calculate the change in the entropy of the universe with this process.

Solution:

Initial state of the steam: superheated at 0.2 MPa and 200°C
 $h_1 = 2870.4$ kJ/kg; and $s_1 = 7.5033$ kJ/kgK

Final state: saturated liquid at 0.2 MPa.
 $h_2 = 504.52$ kJ/kg and $s_2 = 1.5295$ kJ/kgK

Hence $\Delta S_{\text{steam}} = s_2 - s_1 = 1.5295 - 7.5033 = -5.9738$ kJ/kgK

For a constant pressure process: $q = \Delta h$

Therefore, $q = h_2 - h_1 = 504.52 - 2870.4 = -2365.68$ kJ

Entropy change of the surroundings = $\Delta S_{\text{sur}} = Q/T_{\text{sur}} = 2365.88/300 = 7.886$ kJ/K

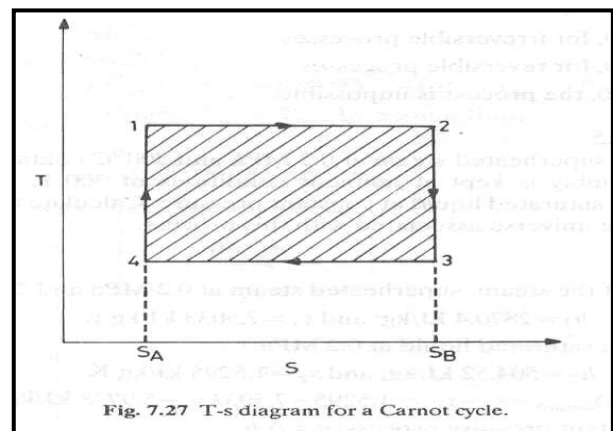
Hence, $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = -5.9738 + 7.886 = 1.9122$ kJ/K

$\Delta S_{\text{uni}} > 0$ and hence the process is irreversible and feasible.

Temperature-Entropy diagram

Entropy change of a system is given by $dS = (dQ/T)_R$. during energy transfer as heat to the system from the surroundings is given by $dQ = TdS$. Hence if T and S are chosen as

independent variables, then the integral $\int TdS$ is the area under the curve.



The first law of thermodynamics gives

$$dU = dQ - dW$$

also for a reversible process,

$$dQ = TdS \text{ and } dW = PdV$$

$$\text{Therefore, } dU = TdS - PdV$$

For a cyclic process, the above equation reduces to $\oint TdS = \oint PdV$

For a cyclic process, $\oint TdS$ represents the net heat interaction which is equal to the net work done by the system. Hence **the area enclosed by a cycle on a T-S diagram represents the net work done by a system.**

Second law analysis of a control volume

$$dS \geq dQ/T$$

where the equality sign holds good for reversible processes and the inequality sign holds good for all irreversible processes. This can be expressed as

$$\Delta S = dQ/T + S_G$$

where S_G represents the entropy generation in the system and it cannot take a negative value. $S_G = 0$ for a reversible process

$S_G > 0$ for an irreversible process

Consider a control volume through which material flows continuously in and out. At time, t , the system constitutes both the mass inside the control volume and the mass about to enter the control volume during a small time interval dt .

The entropy of the system
$$= m(t)s(t) + \dot{m}_i s_i dt$$
$$= S(t) + \dot{m}_i s_i dt$$

At time $(t+dt)$ the entropy of the system

$$= m(t+dt)s(t+dt) + \dot{m}_e s_e dt = S(t+dt) + \dot{m}_e s_e dt$$

where,

$m(t)$ = mass inside the control volume at time t

$s(t)$ = specific entropy of matter inside the control volume at time t

$m(t+dt)$ = mass inside the control volume at time $(t+dt)$

$s(t+dt)$ = specific entropy of the mass inside the control volume at time $(t+dt)$

$S(t+dt)$ = entropy of control volume at time $(t+dt)$

Then,

$$\left[S(t+dt) + \dot{m}_e s_e dt \right] - \left[S(t) + \dot{m}_i s_i dt \right] = \dot{Q} dt / T + \dot{S}_G dt$$

$$\frac{S(t+dt) - S(t)}{dt} + \dot{m}_e s_e - \dot{m}_i s_i = \dot{Q} / T + \dot{S}_G$$

$$\text{or, } dS / dt + \dot{m}_e s_e - \dot{m}_i s_i = \dot{Q} / T + \dot{S}_G$$

This can be rearranged as :

$$dS / dt = (\dot{m}_i s_i + \dot{Q} / T) - (\dot{m}_e s_e) + \dot{S}_G$$

or stated in words:

[The rate of accumulation of entropy] = [Rate of inflow of entropy] – [Rate of outflow of entropy] + [Rate of generation of entropy]

Example:

An inventor claims to have designed a device which takes in 2 kmol/s of air at 250 kPa and 350 K and delivers equal amounts of hot stream of air at 100 kPa and 400 K as also a cold stream of air at 100 kPa and 250 K. He further claims that

his device does not require any additional energy as heat or work to operate. Judge whether such a device is feasible or not. Consider air to be an ideal gas with $C_p = 7R/2$

Solution:

The first law of thermodynamics for a control volume gives:

$$\dot{m}_i h_i = \dot{m}_{e1} h_{e1} + \dot{m}_{e2} h_{e2}$$

$$\text{or } 2h_i = h_{e1} + h_{e2}$$

$$\text{or } (h_i - h_{e1}) + (h_i - h_{e2}) = 0$$

$$C_p(T_i - T_{e1}) + C_p(T_i - T_{e2}) = 0$$

$$(350 - 450) + (350 - 250) = 0$$

The first law is thus satisfied.

The second law of thermodynamics gives:

$$\dot{m}_{e1} s_{e1} + \dot{m}_{e2} s_{e2} \geq \dot{m}_i s_i$$

his device does not require any additional energy as heat or work to operate. Judge whether such a device is feasible or not. Consider air to be an ideal gas with $C_p = 7R/2$

Solution:

The first law of thermodynamics for a control volume gives:

$$\dot{m}_i h_i = \dot{m}_{e1} h_{e1} + \dot{m}_{e2} h_{e2}$$

$$\text{or } 2h_i = h_{e1} + h_{e2}$$

$$\text{or } (h_i - h_{e1}) + (h_i - h_{e2}) = 0$$

$$C_p(T_i - T_{e1}) + C_p(T_i - T_{e2}) = 0$$
$$(350 - 450) + (350 - 250) = 0$$

The first law is thus satisfied.

The second law of thermodynamics gives:

$$\dot{m}_{e1} s_{e1} + \dot{m}_{e2} s_{e2} \geq \dot{m}_i s_i$$

The material balance gives

$$m_{e1} + m_{e2} = m_i$$

$$\text{Therefore } (m_{e1}s_{e1} + m_{e2}s_{e2}) \geq (m_{e1} + m_{e2})s_i$$

$$\text{Or, } m_{e1}(s_{e1} - s_i) + m_{e2}(s_{e2} - s_i) \geq 0$$

The change in entropy is given by

$$\Delta s = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

hence,

$$m_{e1}(s_{e1} - s_i) = C_p \ln(450/350) - R \ln(100/250)$$

and,

$$m_{e2}(s_{e2} - s_i) = C_p \ln(250/350) - R \ln(100/250)$$

then,

$$m_{e1}(s_{e1} - s_i) + m_{e2}(s_{e2} - s_i) = 12.7581 \text{ kJ/K} > 0$$

Hence it satisfies the second law of thermodynamics also Therefore the device is feasible.

Thermodynamic relations

Gibbs Function and Helmholtz Function

Gibbs equation is

$$du = Tds - Pdv$$

The enthalpy h can be differentiated,

$$dh = du + pdv + vdP$$

Combining the two results in

$$dh = Tds + vdP$$

The coefficients T and v are partial derivative of $h(s,P)$,

$$\left(\frac{\partial h}{\partial s} \right)_P = T$$

$$\left(\frac{\partial h}{\partial P} \right)_s = v$$

Since $v > 0$, an isentropic increase in pressure will result in an increase in enthalpy.

We introduce Helmholtz function

$$a = u - Ts$$

Combine Gibbs equation with the differential of a ,

$$da = -Pdv - sdT$$

The coefficient $-P$ and $-s$ are the partial derivatives of $f(v,T)$, so

$$\left(\frac{\partial a}{\partial v} \right)_T = -P$$

$$\left(\frac{\partial a}{\partial T} \right)_v = -s$$

Similarly, using the Gibbs function

$$g = h - Ts$$

$$dg = vdP - sdT$$

Consequently,

$$\left(\frac{\partial g}{\partial P}\right)_T = v$$

$$\left(\frac{\partial g}{\partial T}\right)_P = -s$$

Note:

1. The decrease in Helmholtz function of a system sets an upper limit to the work done in any process between two equilibrium states at the same temperature during which the system exchanges heat only with a single reservoir at this temperature. Since the decrease in the Helmholtz potential represents the potential to do work by the system, it is also a thermodynamic potential.

2. The decrease in Gibbs function of a system sets an upper limit to the work, exclusive of “pdv” work in any process between two states at the same temperature and pressure, provided the system exchanges heat only with a single reservoir at this temperature and that the surroundings are at a constant pressure equal to that in the end states of the process.

The maximum work is done when the process is isothermal isobaric. Gibbs function is also called Chemical Potential.

Some important property relations

$$dz(x,y) = Mdx + Ndy$$

$$\text{where, } M = \left(\frac{\partial z}{\partial x}\right)_y \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

Mathematically, we would say that dz is an exact differential, which simply means that z is a continuous function of the two independent variables x and y . Since the order in which a second partial derivative is taken is unimportant, it follows that,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Maxwell's relations:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad [\text{From equation } du = Tds - Pd v]$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \quad [\text{From equation } dh = Tds + v dP]$$

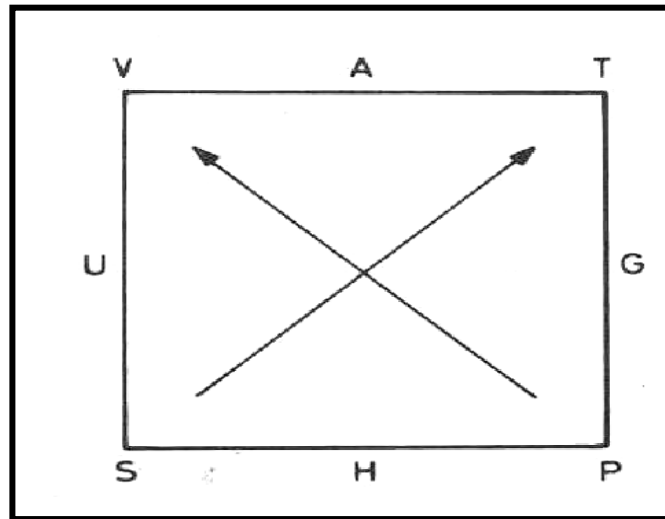
$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad [\text{From equation } da = -Pd v - s dT]$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \quad [\text{From equation } dg = v dP - s dT]$$

Mnemonic Diagram

The differential expressions for the thermodynamic potentials and Maxwell relations can be remembered conveniently in terms of a thermodynamic Mnemonic diagram.

The diagram consists of a square with two diagonal arrows pointing upwards and the thermodynamic potentials in alphabetical order clockwise on the sides as shown in figure. The natural variables associated with each potential are placed in the corners.



Diagonal arrows indicate the coefficients associated with the natural variables in the differential expression of the potential. The sign of the coefficient depends on whether the arrow is pointing towards (-ve) or away from the natural variable (+ve).

For example,

$$du = (\text{sign})(\text{coeff.}) ds + (\text{sign})(\text{coeff.}) dv$$

$$du = (\text{sign})Tds + (\text{sign})Pdv$$

$$du = +Tds - Pdv$$

To write the Maxwell relations we need to concentrate on the direction of the arrows and the natural variables only.

If both the arrows pointing in the same direction, there is no need to change the sign, otherwise the equation should carry a negative sign.

The internal energy

$$u = u(T, v)$$

For a simple compressible substance,

$$du = C_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

$$ds = \frac{C_v}{T} dT + \frac{1}{T} \left[\left(\frac{\partial u}{\partial v} \right)_T + P \right] dv$$

Taking entropy as a function of temperature and volume,

$$\left(\frac{\partial s}{\partial T} \right)_v = \frac{C_v}{T}$$

Using third Maxwell's relation,

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v = \frac{1}{T} \left[\left(\frac{\partial u}{\partial v} \right)_T + P \right]$$

From this we obtain

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P$$

This important equation expresses the dependence of the internal energy on the volume at fixed temperature solely in terms of measurable T, P and v. This is helpful in construction of tables for u in terms of measured T, P and v.

For a perfect gas,

$$Pv = RT$$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v}$$

$$\left(\frac{\partial u}{\partial v} \right)_T = T \frac{R}{v} - P = P - P = 0$$

This implies that, for a perfect gas, internal energy is independent of density and depends only on T.

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv$$

Similarly it can be shown using Fourth Maxwell's relation that

$$ds = \frac{C_p}{T} dT + \left(\frac{\partial v}{\partial T} \right)_p dP$$

Using the above two equations and solving for dP,

$$dP = \frac{C_p - C_v}{T(\partial v / \partial T)_p} dT - \frac{(\partial P / \partial T)_v}{(\partial u / \partial T)_p} dv$$

Considering P as a function of T and v, we see that

$$\frac{C_p - C_v}{T(\partial v / \partial T)_p} = \left(\frac{\partial P}{\partial T} \right)_v$$

Two thermodynamic properties can be defined at this stage,

$$\beta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad \kappa \equiv -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$$

β is called the isobaric compressibility and κ is called the isothermal compressibility.

From calculus, it can be shown that,

$$\left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_P \left(\frac{\partial v}{\partial P} \right)_T = -1$$

or,

$$\left(\frac{\partial P}{\partial T} \right)_v = -\frac{(\partial v / \partial T)_P}{\left(\frac{\partial v}{\partial P} \right)_T} = \frac{\beta}{\kappa}$$

Therefore,

$$C_p - C_v = -\frac{T \left[(\partial v / \partial P)_T \right]^2}{(\partial v / \partial P)_T}$$

Since $(\partial v / \partial P)_T$ is always negative for all stable substances, C_p is always greater than C_v

Available and Unavailable Energy

The second law of thermodynamics tells us that it is not possible to convert all the heat absorbed by a system into work.

Suppose a certain quantity of energy Q as heat can be received from a body at temperature T.

The maximum work can be obtained by operating a Carnot engine (reversible engine) using the body at T as the source and the ambient atmosphere at T_0 as the sink.

$$W = Q\eta = Q \left(1 - \frac{T_0}{T} \right) = Q - T_0 |\Delta s|$$

Where Δs is the entropy of the body supplying the energy as heat.

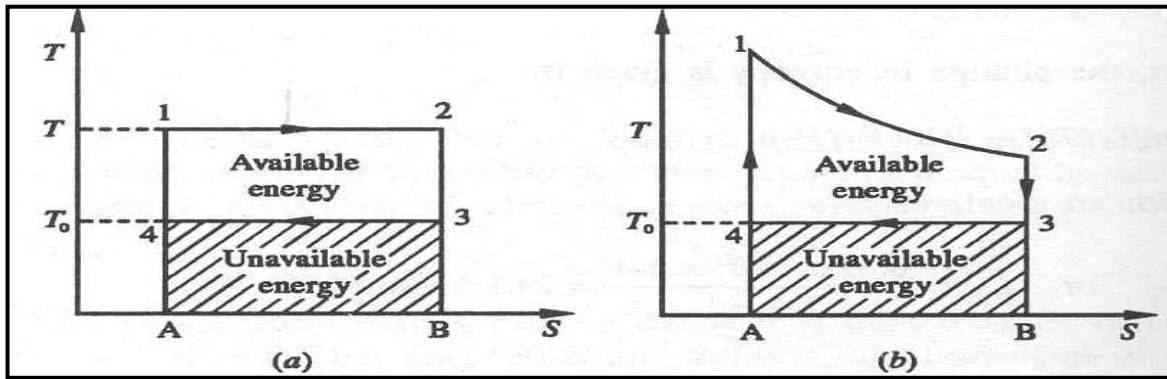
The Carnot cycle and the available energy is shown in figure.

The area 1-2-3-4 represents the available energy.

The shaded area 4-3-B-A represents the energy, which is discarded to the ambient atmosphere, and this quantity of energy cannot be converted into work and is called *Unavailable energy*.

Suppose a finite body is used as a source. Let a large number of differential Carnot engines be used with the given body as the source.

$$dW = dQ\eta = dQ\left(1 - \frac{T_0}{T}\right)$$



If the initial and final temperatures of the source are T_1 and T_2 respectively, the total work done or the available energy is given by

$$W = \int dQ\eta = \int_{T_1}^{T_2} dQ\left(1 - \frac{T_0}{T}\right) = Q - T_0 \int_{T_1}^{T_2} \frac{dQ}{T}$$

$$\text{or } W = Q - T_0 |\Delta s|$$

Loss in Available Energy

Suppose a certain quantity of energy Q is transferred from a body at constant temperature T_1 to another body at constant temperature T_2 ($T_2 < T_1$).

Initial available energy, with the body at T_1 ,

$$= Q\left(1 - \frac{T_0}{T_1}\right)$$

Final available energy, with the body at T_2 ,

$$= Q\left(1 - \frac{T_0}{T_2}\right)$$

Loss in available energy

$$= Q\left(1 - \frac{T_0}{T_1}\right) - Q\left(1 - \frac{T_0}{T_2}\right) = T_0\left(\frac{Q}{T_2} - \frac{Q}{T_1}\right) = T_0\Delta s_{uni}$$

where Δs_{uni} is the change in the entropy of the universe.

Availability Function

The availability of a given system is defined as *the maximum useful work that can be obtained in a process in which the system comes to equilibrium with the surroundings or attains the dead state.*

(a) Availability Function for Non-Flow process:-

Let P_0 be the ambient pressure, V_1 and V_0 be the initial and final volumes of the system respectively.

If in a process, the system comes into equilibrium with the surroundings, the work done in pushing back the ambient atmosphere is $P_0(V_0 - V_1)$.

$$\text{Availability} = W_{\text{useful}} = W_{\text{max}} - P_0(V_0 - V_1)$$

Consider a system which interacts with the ambient at T_0 . Then,

$$W_{\text{max}} = (U_1 - U_0) - T_0(S_1 - S_0)$$

$$\begin{aligned} \text{Availability} &= W_{\text{useful}} = W_{\text{max}} - P_0(V_0 - V_1) \\ &= (U_1 - T_0 S_1) - (U_0 - T_0 S_0) - P_0(V_0 - V_1) \\ &= (U_1 + P_0 V_1 - T_0 S_1) - (U_0 + P_0 V_0 - T_0 S_0) \\ &= \phi_1 - \phi_0 \end{aligned}$$

where $\phi = U + P_0 V - T_0 S$ is called the availability function for the non-flow process. Thus, the availability: $\phi_1 - \phi_0$

If a system undergoes a change of state from the initial state 1 (where the availability is $(\phi_1 - \phi_0)$) to the final state 2 (where the availability is $(\phi_2 - \phi_0)$), the change in the availability or the change in maximum useful work associated with the process, is $\phi_1 - \phi_2$.

(b) Availability Function for Flow process:-

The maximum power that can be obtained in a steady flow process while the control volume exchanges energy as heat with the ambient at T_0 , is given by:

$$\begin{aligned} W_{sh(\text{max})} &= (H_1 - H_0) - T_0(S_1 - S_0) \\ W_{sh(\text{max})} &= (H_1 - T_0 S_1) - (H_0 - T_0 S_0) \end{aligned}$$

Sometimes the availability for a flow process is written as:

$$\begin{aligned} W_{\text{useful}} &= B_1 - B_0 \\ \text{where, } B &= H - T_0 S \end{aligned}$$

which is called the **Darrieus Function**.

Work Potential Associated with Internal Energy

The total useful work delivered as the system undergoes a reversible process from the given state to the dead state (that is when a system is in thermodynamic equilibrium with the environment), which is *Work potential* by definition.

$$\text{Work Potential} = W_{\text{useful}} = W_{\text{max}} - P_0(V_0 - V_1)$$

$$\begin{aligned}
&= (U_1 - T_0 S_1) - (U_0 - T_0 S_0) - P_0(V_0 - V_1) \\
&= (U_1 + P_0 V_1 - T_0 S_1) - (U_0 + P_0 V_0 - T_0 S_0) \\
&= \phi_1 - \phi_0
\end{aligned}$$

The work potential of internal energy (or a closed system) is either positive or zero. It is never negative.

Work Potential Associated with Enthalpy, h

The work potential associated with enthalpy is simply the sum of the energies of its components.

$$\begin{aligned}
W_{sh(max)} &= (H_1 - H_0) - T_0(S_1 - S_0) \\
W_{sh(max)} &= (H_1 - T_0 S_1) - (H_0 - T_0 S_0)
\end{aligned}$$

The useful work potential of Enthalpy can be expressed on a unit mass basis as:

$$w_{sh} = (h_1 - h_0) - T_0(s_1 - s_0)$$

here h_0 and s_0 are the enthalpy and entropy of the fluid at the dead state. The work potential of enthalpy can be negative at sub atmospheric pressures.

UNIT-III

PURE SUBSTANCES AND GAS LAWS

The term saturation temperature designates the temperature at which vaporization takes place.

For water at 99.6 C the saturation pressure is 0.1 M Pa, and for water at 0.1 Mpa, the saturation temperature is 99.6 C.

If a substance exists as liquid at the saturation temperature and pressure it is called saturated liquid.

If the temperature of the liquid is lower than saturation temperature at the existing pressure it is called sub-cooled liquid or compressed liquid.

1. When a substance exists as part liquid and part vapor at the saturation temperature, its quality is defined as the ratio of the mass of vapor to the total mass.
2. If a substance exists as vapor at the saturation temperature, it is called a saturated vapor.
3. When the vapor is at a temperature greater than the saturation temperature, it is said to exist as superheated vapor.
4. At the critical point, the saturated liquid and saturated vapor state are identical.
5. At supercritical pressures, the substance is simply termed fluid rather than liquid or vapor.
6. If the initial pressure at -20°C is 0.260 kPa, heat transfer results in increase of temperature to -10°C . Ice passes directly from the solid phase to vapor phase.
7. At the triple point (0.6113 kPa) and a temperature of -20°C , let heat transfer increase the temperature until it reaches 0.01°C . At this point, further heat transfer may cause some ice to become vapor and some to become liquid. The three phases may be present simultaneously in equilibrium.

Tables of Thermodynamic Properties

Tables of thermodynamic properties of many substances are available, and in general, all these have same form.

Steam tables are selected because steam is used extensively in power plants and industrial processes.

The steam tables provide the data of useful thermodynamic properties like T, P, v, u, h and s for saturated liquid, saturated vapor and superheated vapor.

Since the properties like internal energy, enthalpy and entropy of a system cannot be directly measured; they are related to change in the energy of the system.

Hence one can determine Δu , Δh , Δs , but not the absolute values of these properties. Therefore it is necessary to choose a reference state to which these properties are arbitrarily assigned some numerical values.

For water, the triple point ($T = 0.01^\circ \text{C}$ and $P = 0.6113 \text{ kPa}$) is selected as the reference state, where the internal energy and entropy of saturated liquid are assigned a zero value. In the saturated steam tables, the properties of saturated liquid that is in equilibrium with saturated vapor are presented.

During phase transition, the pressure and temperature are not independent of each other. If the temperature is specified, the pressure at which both phases coexist in equilibrium is equal to the saturation pressure.

Hence, it is possible to choose either temperature or pressure as the independent variable, to specify the state of two-phase system.

Depending on whether the temperature or pressure is used as the independent variable, the tables are called temperature or pressure tables.

The two phases- liquid and vapor can coexist in a state of equilibrium only up to the critical point.

Therefore the listing of the thermodynamic properties of steam in the saturated steam tables ends at the critical point (374.15°C and 212.2 bar).

If the steam exists in only one phase (superheated steam), it is necessary to specify two independent variables, pressure and temperature, for the complete specification of the state. In the superheated steam tables, the properties- v , u , h , and s - are tabulated from the saturation temperature to some temperature for a given pressure.

The thermodynamic properties of a liquid and vapor mixture can be evaluated in terms of its quality. In particular, the specific volume, specific internal energy, specific enthalpy and specific entropy of a mixture of quality X are given by

$$v = (1-X)v_f + Xv_g, u = (1-X)u_f + Xu_g, h = (1-X)h_f + Xh_g = h_f + Xh_{fg}, s = (1-X)s_f + Xs_g$$

where $h_{fg} = h_g - h_f$ = latent heat of vaporization.

Temperature-volume diagram

The locus of all the saturated states gives the saturated liquid curve AC and the locus of all the saturated vapor states gives the saturated vapor curve BC.

The point C represents the critical point. The difference between v_g and v_f reduces as the pressure is increased, and at the critical point $v_g = v_f$.

At the critical point, the two phases-liquid and vapor- are indistinguishable.

Pressure-volume diagram

The pressure-volume (P-V) diagram for a pure substance is shown in Figure. The curves AC and BC represent the saturated liquid curve and saturated vapor curve, respectively, and C is critical point.

The area under the curve represents the two-phase region. Any point M in this region is a mixture of saturated liquid (shown as f) and saturated vapor (g).

Mollier (h-s) Diagram

The h-s diagram was introduced by Richard Mollier and was named after him. It consists of a family of constant pressure lines, constant temperature lines and constant volume lines plotted on enthalpy versus entropy coordinates. In the two-phase region, the constant pressure and constant temperature lines coincide.

Problems on Mollier chart and steam tables

Determine the enthalpy of water at 100° C and 15 MPa (a) by using compressed liquid tables, (b) by approximating it as a saturated liquid, and (c) by using the correction factor.

At 100°C, the saturation pressure of water is 101.35 kPa, and since $P > P_{sat}$, the water exists as a compressed liquid at the specified state.

(a) from the compressed liquid tables,

$$P = 15 \text{ Mpa}, T = 100^\circ\text{C}, h = \mathbf{430.28 \text{ kJ/kg}}$$

This is the exact value.

(b) Approximating the compressed liquid as a saturated liquid at 100°C, as is commonly done, we obtain

$$h = h_{f@100^\circ\text{C}} = \mathbf{419.04 \text{ kJ/kg}}$$

This value is in error by about 2.6 percent.

(c) From equation

$$h_{@P,T} = h_{f@T} + v_{f@T}(P - P_{sat})$$

$$= 419.04 + 0.001(15000 - 101.35) \text{ kJ/kg}$$

$$= \mathbf{434.60 \text{ kJ/kg}}$$

Problem # 1 (Nozzle)

Nitrogen gas flows into a convergent nozzle at 200 kPa, 400 K and very low velocity. It flows out of the nozzle at 100 kPa, 330 K. If the nozzle is insulated, find the exit velocity.

$$V_i = 0$$

Adiabatic nozzle

The SSSF equation:

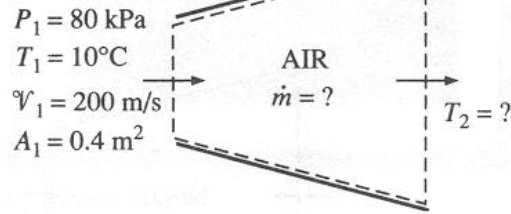
$$\begin{aligned} V_e^2/2 &= (h_i - h_e) = C_p(T_i - T_e) \\ &= \{\gamma R_u / M(\gamma - 1)\} (T_i - T_e) \\ &= \{1.4 * 8314 / (28 * 0.4)\} (400 - 330) \\ &= 72747.5 \text{ m}^2/\text{s}^2 \end{aligned}$$

We get, $V_e = \mathbf{381.44 \text{ m/s}}$

Problem # 2 (Diffuser)

Air at 10° C and 80 kPa enters the diffuser of a jet engine steadily with a velocity of 200 m/s. The inlet area of the diffuser is 0.4 m². The air leaves the diffuser with a velocity that is very small compared with the inlet velocity. Determine (a) the mass flow rate of the air and (b) the temperature of the air leaving the diffuser.

There



Solution:

Assumptions: This is a steady flow process. Air is an ideal gas. The potential energy change is zero. Kinetic energy at diffuser exit is negligible. There are no work interactions. Heat transfer is negligible.

To determine the mass flow rate, we need the specific volume of air.

$$v_1 = RT_1/P_1 = 0.287 \cdot 283 / 80 = 1.015 \text{ m}^3/\text{kg}$$

$$\dot{m} = 1/v_1(V_1 A_1) = (200 \cdot 0.4) / 1.015 = 78.8 \text{ kg/s}$$

For steady flow, mass flow through the diffuser is constant.

$$(b) (h_1 + V_1^2/2) = (h_2 + V_2^2/2) \quad (\text{since } Q = 0, W = 0, \text{ and } \Delta PE = 0)$$

$$h_2 = h_1 - (V_2^2 - V_1^2)/2$$

The exit velocity of a diffuser is very small and therefore neglected.

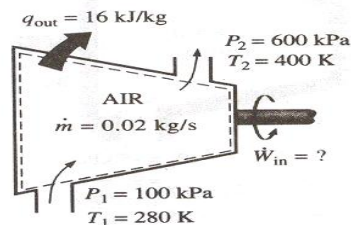
$$h_2 = h_1 + V_1^2/2$$

$$T_2 = T_1 + V_1^2/2C_p$$

$$T_2 = 283 + 200^2/(2 \cdot 1004) \\ = 302.92 \text{ K}$$

Compressing air by a compressor

Air at 100 kPa and 280 K is compressed steadily to 600 kPa and 400 K. The mass flow rate of air is 0.02 kg/s and a heat loss of 16 kJ/kg occurs during the process. Assuming the changes in KE and PE are negligible, determine the necessary power input to the compressor.



We take the compressor as the system. This is a control volume since the mass crosses the system boundary during the process. Heat is lost from the system and work is supplied to the system. With similar assumptions as in the diffuser problem,

$$w = q + (h_2 - h_1)$$

$$\text{The input power} = m (q + (h_2 - h_1))$$

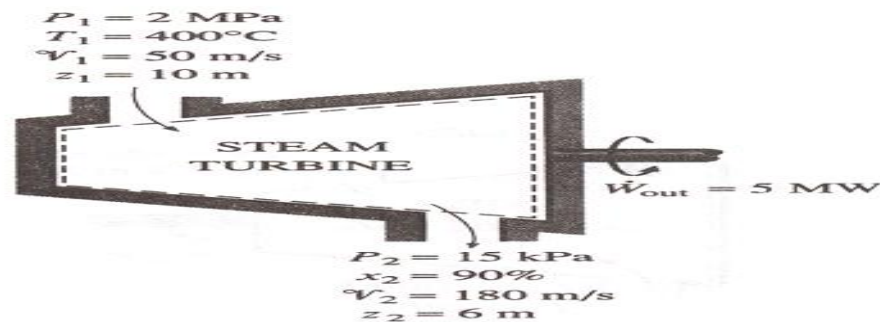
$$= 0.02 (16 + (1.004 * (400 - 280)))$$

$$= \mathbf{2.73 \text{ kW}}$$

Power generation by a steam turbine

The power output of an adiabatic steam turbine is 5 MW, and the inlet and exit conditions of the steam are as indicated in the figure.

- Compare the magnitude of Δh , ΔKE , and ΔPE
- Determine the work done per unit mass of the steam flowing through the turbine
- Calculate the mass flow rate of the steam.



We take the turbine as a system. The control volume is shown in the figure. The system, the inlet and exit velocities do work and elevations are given and thus the kinetic and potential energies are to be considered.

At the inlet, the steam is in superheated vapor state.

$$h_1 = 3247.6 \text{ kJ/kg.}$$

At the turbine exit, we have a saturated liquid-vapor mixture at 15 kPa pressure. The enthalpy at this state is

$$h_2 = h_f + x_2 h_{fg}$$

$$= 225.94 + 0.9 * 2373.1$$

$$= 2361.73 \text{ kJ/kg}$$

$$\Delta h = h_2 - h_1$$

$$= 2361.73 - 3247.6 = \mathbf{-885.87 \text{ kJ/kg}}$$

$$\Delta ke = (V_2^2 - V_1^2)/2 = (180^2 - 50^2)/2 * 1000$$

$$= \mathbf{14.95 \text{ kJ/kg}}$$

$$\Delta Pe = g(Z_2 - Z_1) = 9.807 * (6 - 10)/1000$$

$$= \mathbf{-0.04 \text{ kJ/kg}}$$

$$w_{out} = -[(h_2 - h_1) + (V_2^2 - V_1^2)/2 + g(Z_2 - Z_1)]$$

$$= -[-885.87 + 14.95 - 0.04]$$

$$= \mathbf{870.96 \text{ kJ/kg}}$$

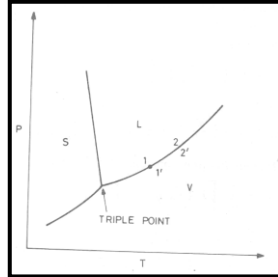
(d) The required mass flow rate for a 5MW power output is $5000/870.96 = \mathbf{5.74 \text{ kg/s}}$

Clapeyron Equation

To find out the dependence of pressure on equilibrium temperature when two phases coexist. Along a phase transition line, the pressure and temperature are not independent of each other, since the system is univariant, that is, only one intensive parameter can be varied independently. When the system is in a state of equilibrium, i.e., thermal, mechanical and chemical equilibrium, the temperature of the two phases has to be identical, the pressure of the two phases has to be equal and the chemical potential also should be the same in both the phases. Representing in terms of Gibbs free energy, the criterion of equilibrium is:

$$d\hat{g} = 0 \text{ at constant T and P}$$

$$\text{or, } d\hat{g} = -\hat{s}dT + \hat{v}dP = 0$$



Consider a system consisting of a liquid phase at state 1 and a vapour phase at state 1' in a state of equilibrium. Let the temperature of the system is changed from T_1 to T_2 along the vaporization curve.

For the phase transition for 1 to 1':

$$d\hat{g} = -\hat{s}dT + \hat{v}dP = 0$$

$$\text{or } \hat{g}_{\text{liquidphase}} = \hat{g}_{\text{vaporphase}}$$

$$\text{or } \hat{g}_1 = \hat{g}_2$$

In reaching state 2 from state 1, the change in the Gibbs free energy of the liquid phase is given by:

$$\hat{g}_2 - \hat{g}_1 = -\hat{s}_f dT + \hat{v}_f dP$$

Similarly, the change in the Gibbs free energy of the vapour phase in reaching the state 2' from state 1' is given by:

$$\hat{g}_{2'} - \hat{g}_{1'} = -\hat{s}_g dT + \hat{v}_g dP$$

Therefore, $-\hat{s}_f dT + \hat{v}_f dP = -\hat{s}_g dT + \hat{v}_g dP$

$$\text{Or } \left(\frac{\partial P}{\partial T} \right)_{sat} = \frac{\hat{s}_g - \hat{s}_f}{\hat{v}_g - \hat{v}_f}$$

Where the subscript *sat* implies that the derivative is along the saturation curve.

The entropy change associated with the phase transition:

$$\hat{s}_g - \hat{s}_f = \frac{\hat{h}_g - \hat{h}_f}{T} = \frac{\hat{h}_{fg}}{T}$$

$$\text{Hence, } \left(\frac{\partial P}{\partial T} \right)_{sat} = \frac{\hat{h}_{fg}}{T \hat{v}_{fg}} = \frac{\Delta \hat{h}}{T \Delta \hat{v}}$$

Which is known as the **Clapeyron equation**

Since $\Delta \hat{h}$ is always positive during the phase transition, $\left(\frac{\partial P}{\partial T} \right)_{sat}$ will be positive or negative depending upon whether the transition is accompanied by expansion ($\Delta \hat{v} > 0$) or contraction ($\Delta \hat{v} < 0$).

Consider the liquid-vapour phase transition at low pressures. The vapour phase may be approximated as an ideal gas. The volume of the liquid phase is negligible compared to the volume of the vapour phase ($\hat{v}_g \gg \hat{v}_f$) and hence $\hat{v}_{fg} = \Delta \hat{v} = \hat{v}_g = RT/P$.

The Clapeyron equation becomes:

$$\left(\frac{\partial P}{\partial T} \right)_{sat} = \frac{\hat{h}_{fg} P}{RT^2}$$

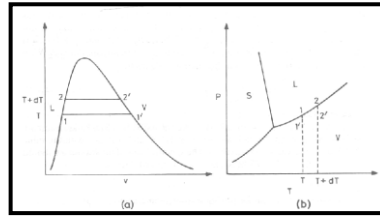
$$\text{or } \frac{d \ln P}{dT} = \frac{\hat{h}_{fg}}{RT^2}$$

which is known as the **Clausius-Clapeyron equation**.

Assume that \hat{h}_{fg} is constant over a small temperature range, the above equation can be integrated

$$\text{to get, } \ln \frac{P_2}{P_1} = \frac{\hat{h}_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \text{ or } \ln P = -\frac{\hat{h}_{fg}}{RT} + \text{constant}$$

Hence, a plot of $\ln P$ versus $1/T$ yields a straight line the slope of which is equal to $-(h_{fg}/R)$.



For a solid-to-liquid transition, it is a reasonably good approximation to assume that the molar heat capacity and the molar volume are constant in each phase and the coefficient of volume expansion β is negligible for each phase. Then,

$$\frac{\partial (\hat{h}_{sf}/T)}{\partial T} = \frac{\hat{C}_{pf} - \hat{C}_{ps}}{T}$$

where \hat{h}_{sf} is the latent heat of fusion.

For the transition from liquid phase to vapour phase, the molar volume of the liquid phase can be neglected compared to the molar volume of the gas phase, and $\beta_g \gg \beta_f$. The vapour phase may be approximated as an ideal gas. Then $\beta_g = 1/T$. It is clear that $v_g \beta_g > v_f \beta_f$. Hence,

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf})$$

Phase Equilibrium- Gibbs Phase Rule

The number of independent variables associated with a multi component, multiphase system is given by the **Gibbs Phase Rule**, expressed as,

$$F = C - P + 2$$

Where,

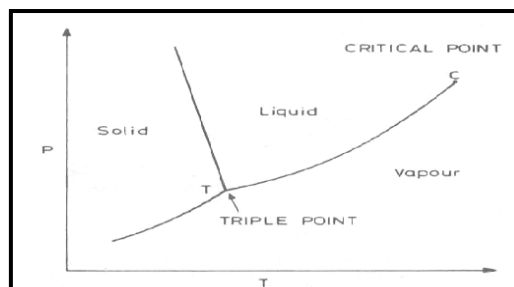
F= The number of independent variables

C= The number of components

P= The number of phases present in the equilibrium

- For a single component (C=1) two phase (P=2) system, one independent intensive property needs to be specified (F=1).
- At the triple point, for C=1, P=3 and thus F=0. None of the properties of a pure substance at the triple point can be varied.
- Two independent intensive properties need to be specified to fix the equilibrium state of a pure substance in a single phase.

Phase diagram for a single component system is given in figure.



Problems on steam tables

A systematic approach to problem solving

Step 1. Identify the system and draw a sketch of it. The system that is about to be analyzed should be identified on the sketch by drawing its boundaries using the dashed lines.

Step 2. List the given information on the sketch. Heat and work interactions if any should also be indicated on the sketch with proper directions.

Step 3. State any assumptions:

The simplifying assumptions that are made to solve a problem should be stated and fully justified.

Commonly made assumptions:

- (a) Assuming process to be quasi-equilibrium
- (b) Neglecting PE and KE
- (c) Treating gas as ideal
- (d) Neglecting heat transfer from insulated systems.

Step 5. Apply the conservation equations.

Step 6. Draw a process diagram.

Determine the required properties and unknowns.

Problem # 1 A 0.1 m^3 rigid tank contains steam initially at 500 kPa and 200°C . The steam is now allowed to cool until the temperature drops to 50°C . Determine the amount of heat transfer during this process and the final pressure in the tank.

State 1: $P_1 = 500 \text{ kPa}$, $T_1 = 200^\circ\text{C}$

$$v_1 = 0.4249 \text{ m}^3/\text{kg}, u_1 = 2642.9 \text{ kJ/kg}$$

State 2: $v_2 = v_1 = 0.4269 \text{ m}^3/\text{kg}$

$$T_2 = 50^\circ\text{C} \rightarrow v_f = 0.001 \text{ m}^3/\text{kg}$$

$$v_g = 12.03 \text{ m}^3/\text{kg}$$

$$u_f = 209.32 \text{ kJ/kg}$$

$$u_g = 2443.5 \text{ kJ/kg}$$

$$P_2 = P_{sat} @ 50^\circ\text{C} = 12.349 \text{ kPa}$$

$$v_2 = v_f + x_2 v_{fg}$$

$$0.4249 = 0.001 + x_2(12.03 - 0.001)$$

$$x_2 = 0.0352$$

$$\begin{aligned}
 u_2 &= u_f + x_2 u_g \\
 &= 209.32 + (0.0352)(2443.5 - 209.32) \\
 &= 288.0 \text{ kJ/kg}
 \end{aligned}$$

$$\begin{aligned}
 m &= V/u = (0.1 \text{ m}^3/\text{kg}) / (0.4249 \text{ m}^3/\text{kg}) \\
 &= 0.235 \text{ kg}
 \end{aligned}$$

$$\begin{aligned}
 -Q_{out} &= \Delta U = m(u_2 - u_1) \\
 Q_{out} &= m(u_1 - u_2) \\
 &= (0.235)(2642.9 - 288) = 553.4 \text{ kJ}
 \end{aligned}$$

Problem # 2 A piston/cylinder contains 50 kg of water at 200 kPa with a volume of 0.1 m^3 . Stop in the cylinder is placed to restrict the enclosed volume to 0.5 m^3 . The water is now heated until the piston reaches the stops. Find the necessary heat transfer.

At 200 kPa,

$$v_f = 0.001061 \text{ m}^3/\text{kg}$$

$$v_{fg} = 0.88467 \text{ m}^3/\text{kg}$$

$$h_f = 504.68 \text{ kJ/kg}$$

$$h_{fg} = 2201.96 \text{ kJ/kg}$$

This is a constant pressure process. Hence,

$$Q = \Delta H$$

The specific volume initially,

$$v_i = 0.1 / 50 = 0.002 \text{ m}^3/\text{kg}$$

$$v = v_f + x v_{fg}$$

$$= 0.001061 + x (0.88467)$$

$$\begin{aligned}
 \text{Therefore, } x &= (0.002 - 0.001061) / 0.88467 \\
 &= 0.001061
 \end{aligned}$$

$$h = h_f + x h_{fg}$$

$$= 504.68 + 0.001061(2201.96)$$

$$= 507.017 \text{ kJ/kg}$$

$$v_{final} = 0.5 / 50 = 0.01 \text{ m}^3/\text{kg}$$

$$v = v_f + x v_{fg}$$

$$\begin{aligned}
 \text{Therefore, } x &= (0.01 - 0.001061) / 0.88467 \\
 &= 0.01
 \end{aligned}$$

$$h_{final} = 504.68 + 0.01(2201.96)$$

$$= 526.69 \text{ kJ/kg}$$

$$Q = \Delta H = 50 (526.69 - 507.017)$$

$$= 983.65 \text{ kJ}$$

Problem # 3 A rigid insulated tank is separated into two rooms by a stiff plate. Room A of 0.5 m^3 contains air at 250 kPa, 300 K and room B of 1 m^3 has air at 150 kPa, 1000 K. The plate is removed and the air comes to a uniform state without any heat transfer. Find the final pressure and temperature.

The system comprises of room A and B together. This is a constant internal energy process as there is no heat and work exchange with the surroundings.

$$\begin{aligned}
 m_A &= P_A V_A / RT_A \\
 &= (250 \times 1000 \times 0.5) / (287 \times 300) \\
 &= 1.452 \text{ kg} \\
 m_B &= P_B V_B / RT_B \\
 &= (150 \times 1000 \times 1.0) / (287 \times 1000) \\
 &= 0.523 \text{ kg}
 \end{aligned}$$

$$\Delta U_A + \Delta U_B = 0$$

Let T_f be the final temperature at equilibrium

$$m_A (T_f - 300) + m_B (T_f - 1000) = 0$$

$$1.452 (T_f - 300) + 0.523 (T_f - 1000) = 0$$

$$T_f = 485.37 \text{ K}$$

$$\begin{aligned}
 P_f &= (1.452 + 0.523) \times 287 \times 485.37 / 1.5 \\
 &= 183.41 \text{ kPa}
 \end{aligned}$$

Problem # 4 A piston / cylinder assembly contains 0.1 m^3 of superheated steam at 10 bar and 400°C . If the steam is allowed to expand reversibly and adiabatically to a pressure of 3 bar, calculate the work done by the steam.

$$\begin{aligned}
 &\text{At 10 bar and } 400^\circ\text{C}, \\
 v &= 0.3065 \text{ m}^3/\text{kg} \\
 h &= 3264.4 \text{ kJ/kg} \\
 s &= 7.4665 \text{ kJ/kg K}
 \end{aligned}$$

At 3 bar,

$$s_g = 6.9909 \text{ kJ/kg K}$$

This is an isentropic process as initial entropy value is greater than s_g at 3 bar, the steam is superheated at the end of the process.

$$\begin{aligned}
 &\text{At 3 bar and } 200^\circ\text{C}, \\
 s &= 7.3119 \text{ kJ/kg K and} \\
 &\text{at } 300^\circ\text{C}, s = 7.7034 \text{ kJ/kg K}
 \end{aligned}$$

therefore, the final state is having a temperature between 200°C and 300°C .

Equating $s_i = s_{\text{final}}$,

Find the enthalpy and specific volume by interpolation. Then calculate u_i and u_{final} .

$$\text{The work done} = \Delta U = m(u_i - u_{\text{final}})$$

GASLAWS

Ideal and Real Gases

Pure Substance: A pure substance is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase but chemical composition is the same in all phases.

Some times the mixture of gases, such as air is considered a pure substance as long as there is no change of phase. Further our emphasis will be on simple compressible substances

Early experiments on the **variables of state** (such as T, P, V, and n) showed that only two of these variables of state need to be known to know the state of a sample of matter.

Extensive variables: depend on the amount of substance present. Examples include the volume, energy, enthalpy, and heat capacity.

Intensive variables: do not depend on the amount of substance present. Examples include the temperature and pressure.

Equations of State

An equation of state is an equation which relates the variables of state (T, P, V, and n). It's particularly useful when you want to know the effect of a change in one of the variables of state

Solids and Liquids: If the pressure on a solid or liquid is increased, the volume does not change much. If the temperature is increased, the volume doesn't change much either. Therefore, an appropriate equation of state describing such systems would be: $V(T,P) = \text{constant}$.

Gases: In contrast, changing the pressure or temperature of a gas will have an easily observable effect on the volume of that gas. For an **ideal gas** (no intermolecular interactions and no molecular volume) an appropriate equation of state would be: $V(T,P,n) = (nRT)/P$.

There are many equations of state describing **real gases**. These equations take in consideration molecular volume and interactions. The most well-known such equations is probably the Van der Waals equation.

Ideal and real gases

An ideal gas is one which follows the ideal gas equation of state, namely

$$PV = (m/M) (MR) T = n R_u T$$

The universal gas constant has a value of 8.314 J/mol K or kJ/kmol K and is related to the specific gas constant by the relation $R_u = (R / M)$

The ideal gas equation of state can be derived from the kinetic theory of gases where the following assumptions are made:

The molecules are independent of each other. In other words, there are no attractive forces between the molecules.

The molecules do not occupy any volume. That is the volume occupied by the molecules is quite negligible compared to the volume available for motion of the molecules.

The internal energy of an ideal gas is a function of temperature only and is independent of pressure and volume. That is,

$$u = u(T)$$

$$(\partial u / \partial P)_T = 0, (\partial u / \partial v)_T = 0$$

Enthalpy and specific heat

$$h = u + Pv$$

For an ideal gas $u = u(T)$ only and $PV = mRT$ and hence $h = h(T)$ only.

The specific heat at constant volume is defined as the amount of energy transferred as heat at constant volume, per unit mass of a system to raise its temperature by one degree. That is,

$$C_v = (dq/dT)_v$$

The specific heat at constant pressure is defined as the energy transferred as heat at constant pressure, per unit mass of a substance to raise its temperature by one degree. That is $C_p = (dq/dT)_p$

For a constant pressure process $dq = du + dw = du + Pd v = du + Pd v + v dP$ (since $dP=0$ for a constant pressure process)

$$\text{Or } dq = du + d(Pv) = d(U + Pv) = dh$$

$$\text{or } dq = dh$$

$$C_p = (\partial h / \partial T)_p$$

The ratio of specific heat (γ) is given by

$$\gamma = C_p / C_v$$

For mono-atomic ideal gases $\gamma = 1.67$ and for diatomic gases $\gamma = 1.4$.

Relation between two specific heats:

The two specific heats are related to each other.

$$h = u + Pv \text{ or } dh = du + d(Pv)$$

For an ideal gas, the above equation reduces to

$$dh = du + d(RT) = du + R dT \text{ or}$$

$$dh/dT = du/dT + R \text{ or } C_p = C_v + R$$

$$\text{or } C_p - C_v = R \text{ for an ideal gas.}$$

$$\gamma = C_p / C_v \text{ or } C_p = R / (\gamma - 1) \text{ and } C_v = R \gamma / (\gamma - 1)$$

Real gases:

The ideal gas law is only an approximation to the actual behavior of gases.

At high densities, that is at high pressures and low temperatures, the behavior of actual or real gases deviate from that predicted by the ideal gas law. In general, at sufficiently low pressures or at low densities all gases behave like ideal gases.

Van der Waals Equation of State

An equation of state taking account the volume occupied by the molecules and the attractive forces between them.

$$(P + a/v^2)(v - b) = RT$$

where a and b are van der Waals constants.

The equation is cubic in volume and in general there will be three values of v for given values of T and P.

However in some range of values of P and T there is only one real value v.

For $T > T_c$ (critical temperature) there will be only one real value of v and for $T < T_c$ there will be three real values.

In Figure, the solid curve represents the value predicted by the van der Waals equation of state and the points represent the experimentally determined values.

It can be observed that at temperatures greater than critical, there is only one real value of volume for a given P and T .

However at temperatures less than the critical, there are three real values of volume for a given value of P and T .

The experimental values differ from those predicted by van der Waals equation of state in region 2345 if $T < T_c$.

One can use the criterion that the critical isotherm (isotherm passing through the critical point) shows a point of inflexion. Stated mathematically

$$(\partial P / \partial v)_{T=T_c} = 0 \text{ and } (\partial^2 P / \partial v^2)_{T=T_c} = 0$$

$$(\partial P / \partial v)_{T=T_c} = -RT_c / (v_c - b)^2 + 2a / v_c^3 = 0$$

or

$$RT_c / (v_c - b)^2 = 2a / v_c^3$$

$$(\partial^2 P / \partial v^2)_{T=T_c} = 2RT_c / (v_c - b)^3 - 6a / v_c^4 = 0$$

or

$$2RT_c / (v_c - b)^3 = 6a / v_c^4$$

Therefore

$$2 / (v_c - b) = 3 / v_c \text{ or } v_c = 3b$$

At the critical point, the van der Waal's equation is given by

$$P_c = RT_c / (v_c - b) - a / v_c^2$$

From these equations,

$$a = 27R^2 T_c^2 / 64 P_c \text{ and } b = RT_c / 8 P_c$$

Compressibility Factor:

The deviation from ideal behavior of a gas is expressed in terms of the compressibility factor Z , which is defined as the ratio of the actual volume to the volume predicted by the ideal gas law.

$$Z = \text{Actual volume} / \text{volume predicted by ideal gas law} = v / RT / P = Pv / RT$$

For an ideal gas $Pv = RT$ and hence $Z = 1$ at all temperatures and pressures.

The experimental P - v - T data is used to prepare the compressibility chart.

Reduced pressure, $P_R = P / P_c$,

Reduced temperature, $T_R = T / T_c$

Reduced volume, $v_R = v / v_c$

Where P_c , T_c and v_c denote the critical pressure, temperature and volume respectively.

These equations state that the reduced property for a given state is the value of this property in this state divided by the value of this same property by at the critical point.

The striking fact is that when such Z versus P_r diagrams are prepared for a number of different substances, all of them very nearly coincide, especially when the substances have simple, essentially spherical molecules.

We need to know only critical temperature and critical pressure to use this basic generalized chart.

In general it can be noted that idealized gas behavior for very low pressures as compared to critical) regardless of temperature. Furthermore, at high temperatures (greater than twice T_c), the ideal-gas model can be assumed to good accuracy to pressures as high as 4-5 times P_c .

UNIT IV

GAS MIXTURES AND PSYCHROMETRY

The properties of a gas mixture obviously depend on the properties of the individual gases (called components or constituents) as well as on the amount of each gas in the mixture.

COMPOSITION OF A GAS MIXTURE MASS AND MOLE FRACTIONS To determine the properties of a mixture, we need to know the composition of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture: either by specifying the number of moles of each component, called molar analysis, or by specifying the mass of each component, called gravimetric analysis.

mixture of ideal gases

Basic assumption is that the gases in the mixture do not interact with each other.

Consider a mixture with components $l = 1, 2, 3, \dots$ with masses $m_1, m_2, m_3, \dots, m_i$ and

with $N_1, N_2, N_3, \dots, N_i, \dots$ number of moles.

The total mixture occupies a volume V , has a total pressure P and temperature T (which is also the temperature of each of the component species)

The total mass

$$m = \sum m_i$$

Total number of mole N

$$N = \sum N_i$$

Mass fraction of species i

$$\phi_i = \frac{m_i}{m}$$

Mole fraction of species i

$$Y_i = \frac{N_i}{N}$$

The mass and number of moles of species i are related by

$$m_i = N_i M_i$$

N_i is the number of moles of species i and M_i is the molar mass of species i
Also to be noted

$$\sum \phi_i = 1 \quad \text{and} \quad \sum Y_i = 1$$

We can also define a molar mass of the mixture as

$$M = \frac{m}{N} = \frac{\sum N_i M_i}{N}$$

or,

$$M = \frac{\sum N_i}{N} M_i$$

or,

$$M = \sum Y_i M_i$$

Dalton 's Law of partial pressure

Total pressure of an ideal gas mixture is equal to the sum of the partial pressures of the constituent components, That is

$$P = \sum P_i$$

P is the total pressure of the mixture

P_i is the partial pressure of species i

= pressure of the species if it existed alone in the given **temperature T** and **volume V**

$$P_i = \frac{N_i \hat{R} T}{V}$$

\hat{R} is the universal gas constant = 8.314 kJ/k mol K

Dalton 's Law

$$P = \sum P_i = \frac{\sum N_i \hat{R} T}{V} = \frac{RT}{V} \sum N_i$$

or

$$P = \frac{N \hat{R} T}{V}$$

The pressure function of species i

$$\frac{P_i}{P} = \frac{N_i \hat{R} T}{V} \frac{V}{N \hat{R} T} = \frac{N_i}{N} = Y_i$$

Therefore,

Pressure fraction = Mole fraction

Amagat's Law:

Volume of an ideal gas mixture is equal to the sum of the partial volumes

$$V = \sum V_i$$

V = total volume of the mixture

V_i = partial volume of the species i

= volume of the species if it existed alone in the given temperature T and pressure P

For an ideal gas

$$V_i = \frac{N_i \hat{R}T}{P}$$

Amagat's Law

$$V = \sum V_i = \frac{\sum N_i \hat{R}T}{P} = \frac{\hat{R}T}{P} \sum N_i = \frac{\hat{R}T}{P} N$$

or

$$V = \frac{N \hat{R}T}{P}$$

The volume fraction of species i

$$\frac{V_i}{V} = \frac{N_i \hat{R}T}{P} \frac{P}{N \hat{R}T} = \frac{N_i}{N} = Y_i$$

or,

$$\frac{V_i}{V} = Y_i$$

Volume fraction = Mole fraction

Mass based analysis is known as gravimetric analysis

Mole based analysis is known as molar analysis

Therodynamic Properties of Mixtures

Internal Energy

$$U = \sum m_i u_i = \sum N_i \hat{u}_i$$

m_i = mass of species i

u_i = specific internal energy of species i

N_i = number of moles of species i

\hat{u}_i = molar internal energy

Similarly we can write about **Enthalpy**

$$H = \sum m_i h_i = \sum N_i \hat{h}_i$$

Entropy

$$S = \sum m_i s_i = \sum N_i \hat{s}_i$$

Specific internal energy of the mixture

$$u = \frac{U}{M} = \frac{\sum m_i u_i}{M} = \frac{\sum m_i}{M} u_i$$

or

$$u = \sum \phi_i u_i$$

ϕ_i = mass fraction of species i

u_i = specific internal energy of species i

Molar internal energy of mixture

$$\hat{u}_i = \frac{U}{N} = \frac{\sum N_i \hat{u}_i}{N} = \frac{\sum N_i}{N} \hat{u}_i = \sum Y_i \hat{u}_i$$

Y_i = mole fraction of species i

\hat{u}_i = molar internal energy of species i

Similarly we can write for specific enthalpy and molar enthalpy

$$h = \sum \phi_i \hat{h}_i \quad \text{and} \quad \hat{h} = \sum Y_i \hat{h}_i$$

We can also write for specific entropy and molar entropy

$$s = \sum \phi_i \hat{s}_i \quad \text{and} \quad \hat{s} = \sum Y_i \hat{s}_i$$

Change in u , h and s

$$\begin{aligned} \Delta u &= \sum \phi_i \Delta u_i = \sum (\phi_i u_i)_2 - \sum (\phi_i u_i)_1 \\ &= \sum \phi_i (u_{i2} - u_{i1}) \end{aligned}$$

Assume ϕ_i remains unchanged

$$\Delta u = \sum \phi_i c_{v_i} \Delta T$$

For ideal gas mixture

$$\Delta u = \Delta T \sum \phi_i c_{v_i}$$

as ΔT is the same for all species as a result of thermodynamics equilibrium or

$$\Delta u = c_v \Delta T$$

Where $c_v = \sum \phi_i c_{v_i}$ = definition of mixture c_v

Similarly it can be shown that

$$\Delta \hat{u} = \hat{c}_v \Delta T$$

Where

$$\hat{c}_v = \sum Y_i \hat{c}_{v_i} = \text{mixture } \hat{c}_v \text{ (molar basis)}$$

Let us also recall that $\sum \phi_i = 1$ and $\sum Y_i = 1$

We can also write similar relations for mixture enthalpy

$$\Delta h = c_p \Delta T$$

Where

$$c_p = \sum \phi_i c_{p_i} \text{ definition of mixture } c_p$$

and

$$\Delta \hat{h} = \hat{c}_p \Delta T$$

Where

$$\hat{c}_p = \sum Y_i \hat{c}_{p_i} \text{ definition of mixture } \hat{c}_p \text{ (molar basis)}$$

Therefore, $\Delta u = c_v \Delta T$ and $\Delta h = c_p \Delta T$. The equations are similar to the equations for a single (ideal gas) species.

Properties of Atmospheric Air

Dry air is a mechanical mixture of the following gases: Oxygen, nitrogen, carbon dioxide, hydrogen, argon, neon, krypton, helium, ozone, and xenon. Dry air is considered to consist of 21% oxygen and 79% nitrogen **by volume**. It consists of 23% oxygen, and 77% nitrogen **by mass**. **Completely dry air does not exist in nature**. Water vapour in varying amount is diffused through it. If P_a and P_w are the **partial pressures of dry air and water vapour** respectively, then by Dalton's law of **partial pressure**

$$P_a + P_w = P$$

Where P is the atmospheric pressure

Mole – fraction of dry air,

$$Y_a = \frac{P_a}{P} = P_a$$

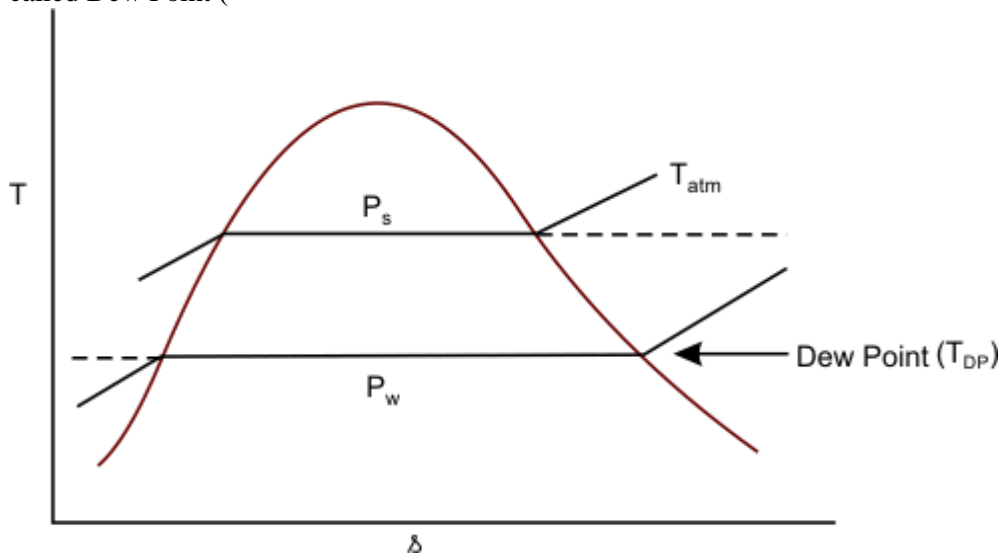
P_m is considered to be 1 atm

Mole – fraction of water vapour,

$$Y_w = \frac{P_w}{P} = P_w$$

Since P_w is very small, the saturation temperature of water vapour at P_w is less than the atmospheric temperature T_{atm} . So the water vapour in air exists in the superheated state, and the air is said to be unsaturated.

If the air- water vapour mixture which is initially not saturated, is cooled at constant pressure, the partial pressure of water vapour in the mixture remains constant till it is equal to the saturation pressure of water. Further cooling result in condensation of water vapour. The temperature at which the vapour condenses when the air-water vapour mixture is cooled at constant pressure, is called Dew Point (



Relative Humidity (RH)

Relative humidity is defined as the ratio of partial pressure of water vapour, P_w , in a mixture to the saturation pressure, P_s , of pure water at the temperature of the mixture

$$RH = \frac{P_w}{P_s} = \phi$$

If water is injected into unsaturated air in a container, water will evaporate, which will increase the moisture content of the air. and P_w will increase. This will continue till the air becomes

saturated at that temperature and there will be no more evaporation of water. For saturated air, relative humidity is 100%. Assuming water vapour as an ideal gas,

$$P_w V = m_w R_{H_2O} T = N_w \bar{R} T$$

$$P_s V = m_s R_{H_2O} T = N_s \bar{R} T$$

And V is the volume and T the temperature of air, the subscripts W and s indicating the unsaturated and saturated states of air respectively.

$$\boxed{RH = \frac{P_w}{P_s} = \frac{m_w}{m_s} = \phi}$$

RH = mass of water vapour in a given volume of air at temperature T / mass of water vapour when the same volume of air is saturated at temperature T

$$= \frac{N_w}{N_s} = \frac{Y_w}{Y_s}$$

Specific Humidity or Humidity Ratio

SH is defined as the **mass of water vapour** per unit **mass of dry air** in a mixture of air and water vapour.

If m_a = mass of dry air, m_w = mass of water vapour

$$SH = \frac{m_w}{m_a} = w$$

Also we know that

$$P_w = m_w R_w T \quad \text{and} \quad P_a V = m_a R_a T$$

$$SH = \frac{m_w}{m_a} = \frac{P_w}{P_a} \cdot \frac{R_a}{R_w} = w$$

or,

$$SH = \frac{P_w}{P_a} \cdot \frac{8.3143/28.96}{8.3143/18} = 0.622 \frac{P_w}{P_a} = w$$

or

$$\boxed{SH = 0.622 \frac{P_w}{(P - P_w)} = w}$$

Where P is the **atmospheric pressure**

Relative humidity,

$$RH = \phi = \frac{P_w}{P_s}$$

$$w = 0.622 \frac{P_w}{P_s} \cdot \frac{P_s}{P_a} = 0.622 \phi \frac{P_s}{P_a}$$

or

$$w = 0.622 \phi \frac{P_s}{P - P_w} = 0.622 \phi \frac{P_s}{P - \phi P_s}$$

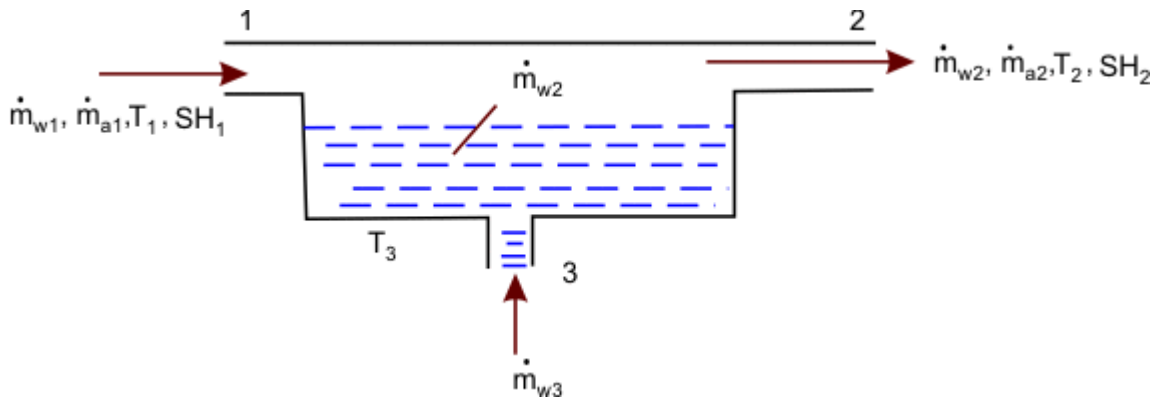
or

$$\phi = \frac{w}{0.622} \cdot \frac{P_g}{P_s}$$

If a mixture of air and superheated (or unsaturated) water vapour is cooled at constant pressure, the partial pressure of each constituent remains constant until the water vapour reaches its saturated state. Further cooling causes condensation. The temperature at which water vapour starts condensing is called the dew point temperature T_{DP} of the mixture. It is equal to the saturation temperature at the partial pressure, P_w of the water vapour in mixture.

ADIABATIC SATURATION

Specific humidity or the relative humidity of an air – water vapour mixture can be measured in principle with the help of a device called the adiabatic saturator



The air – water vapour mixture flows steadily into the device. The SH or w of the incoming mixture has to be determined.

The air – water vapour mixture leaves the adiabatic saturator as saturated mixture. Let the device be insulated so that there is no energy loss.

Since the unsaturated air – water vapour mixture is sweeping over a layer of liquid water, some water evaporates. The energy needed for the evaporation comes from the air mixture. Hence, the air – water vapour mixture leaves the adiabatic saturator at a temperature lower than that of the entering air. As the air leaving the adiabatic saturator is in equilibrium with the liquid water, the temperature of the liquid water is equal to the temperature of the saturated air – water vapour mixture.

Mass balance for air

$$\dot{m}_{a1} = \dot{m}_{a2}$$

Mass balance for water

$$\dot{m}_{w1} + \dot{m}_{w3} = \dot{m}_{w2}$$

Energy balance

$$\dot{m}_{a1}h_{a1} + \dot{m}_{w1}h_{w1} + \dot{m}_{w3}h_{w3} = \dot{m}_{a2}h_{a2} + \dot{m}_{w2}h_{w2}$$

Dividing (35.17) by $\dot{m}_{a1} (= \dot{m}_{a2})$

$$\frac{\dot{m}_{w1}}{\dot{m}_{a1}} + \frac{\dot{m}_{w3}}{\dot{m}_{a1}} = \frac{\dot{m}_{w2}}{\dot{m}_{a2}}$$

$$SH_1 + \frac{\dot{m}_{w3}}{\dot{m}_{a1}} = SH_2$$

$$\dot{m}_{w3} = \dot{m}_{a1} (SH_2 - SH_1)$$

Dividing (35.18) by \dot{m}_{a1}

$$h_{a1} + SH_1 h_{w1} + (SH_2 - SH_1) h_{w3} = h_{a2} + SH_2 h_{w2}$$

or

$$SH_1 = \frac{(h_{a2} - h_{a1}) + SH_2 (h_{w2} - h_{w3})}{(h_{w1} - h_{w3})} = w_1$$

The quantity

$$\begin{aligned} & (h_{a2} - h_{a1}) \\ &= c_p (T_2 - T_1) \end{aligned}$$

Another term, $(h_{w2} - h_{w3})$ has to be estimated properly.

Here h_{w2} refer to the enthalpy of saturated water vapour at temperature T_2 and h_{w3} refers to the enthalpy of the saturated liquid at temperature T_3 or T_2 ($T_2 = T_3$) water pool temperature at steady state is same as T_2)

Therefore

$$(h_{w2} - h_{w3}) = (h_{fg})_2$$

$h_{w1} = h_{g1}$ = enthalpy of the saturated water vapour at state 1

$h_{w3} = h_{f3}$ = enthalpy of the saturated liquid water at temperature T_3 or T_2 , $= h_{f2}$

T_2 does not depend on the temp at which the liquid water enters the device (make-up water temperature)

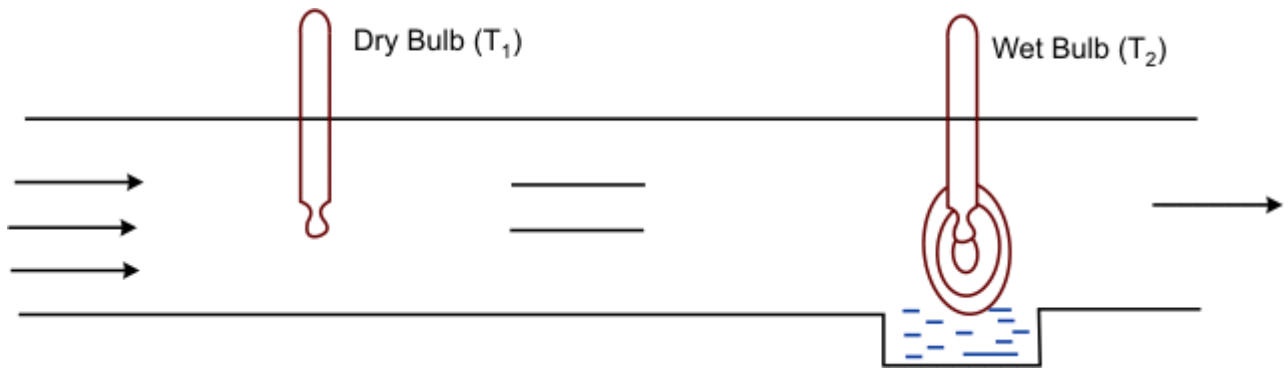
The adiabatic saturation temperature T_2 depends only on the conditions T_1, SH_1 of the entering fluid.

Finally

$$SH = w_1 = \frac{c_p (T_2 - T_1) + w_2 h_{fg2}}{h_{g1} - h_{f2}}$$

Psychrometer

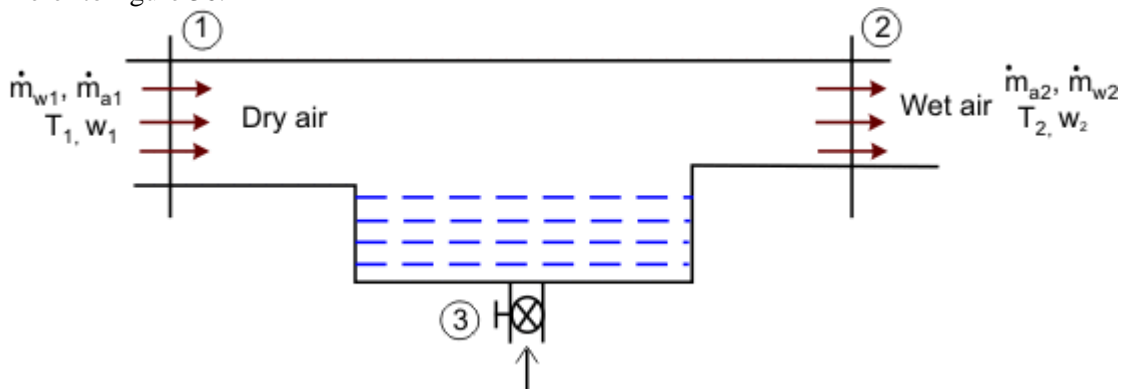
Psychrometer is an instrument to measure the wet-bulb and dry-bulb temperature of an air-water vapour mixture. This instrument uses the **principle of adiabatic saturation**. The specific humidity and relative humidity of air-water vapour mixture can be determined with knowledge of dry-bulb and wet-bulb temperatures figure 36.1



- The dry-bulb temperature is the temperature of the incoming mixture.
- The wet-bulb temperature is the temperature of the saturated air-water vapour mixture.
- For air-water vapour mixtures, the wet-bulb temperature is found to be approximately equal to the adiabatic Saturation temperature (AST).
- If T_1 and T_2 are known, SH_1 & RH_1 can be found out.
- The enthalpy of air-water vapour mixture is expressed as

$$h^* = ha + (SH)hw$$

where hw is the enthalpy of the accompanying water vapour, and $SH = w = \dot{m}_w / \dot{m}_a$
Refer to figure 36.2



We can write

$$h_{a1} + w_1 h_{w1} + (w_2 - w_1) h_{w3} = h_{a2} + w_2 h_{w2}$$

In the above equation, h_{w1} is vapour enthalpy, h_{w2} is also enthalpy of vapour. The term h_{w3} is meant for enthalpy of liquid water $h_{w3} \ll h_{w1}, h_{w2}$

Also $(w_2 - w_1) \ll w_1, w_2$

For the above reasons, we can rewrite (36.2) as

$$h_1 + w_1 h_{w1} = h_{a2} + w_2 h_{w2}$$

Invoking (36.1), the above equation becomes

$$h_1^* = h_2^*$$

h^* is the conserved property in an adiabatic saturation process. (Remember that state 2 need not be saturated). We can further write

$$h^* = h_a + whg$$

Where

$$h_a = c_p T \quad \text{and} \quad whg = h_g(T)$$

If ΔT is small ($\sim 10^\circ\text{C}$), $h_g = \text{constant}$ and we get

$$h^* = c_p T + whg$$

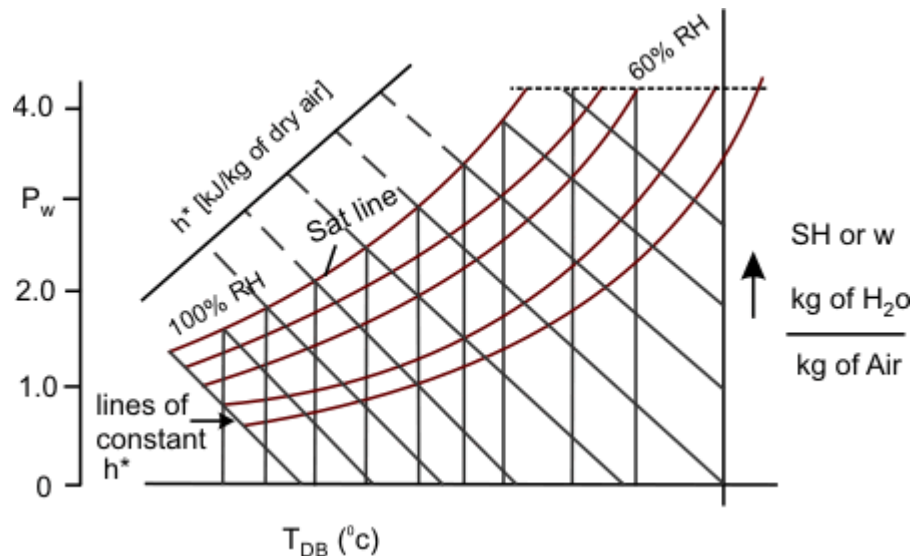
Along an adiabatic miniaturization process h^* will remain constant

$$h_1^* = h_2^*$$

or

$$c_p(T_2 - T_1) + (w_2 - w_1)h_g = 0$$

PSYCHROMETRIC CHART



Abscissa is the dry bulb temperature. The right hand side ordinate provides humidity ratio. The equation shows a direct relationship between w and P_w

$$w = 0.622 \frac{P_w}{P - P_w}$$

Accordingly, the vapour pressure can also be shown as the ordinate. The curves of constant relative humidity are also drawn on the Psychrometric Chart. On figure 36.3, the curves are labeled as $\Phi = 100\%$, 60% etc. Psychrometric Charts also give values of the mixture enthalpy per unit mass of dry air in the mixture. The constant wet bulb

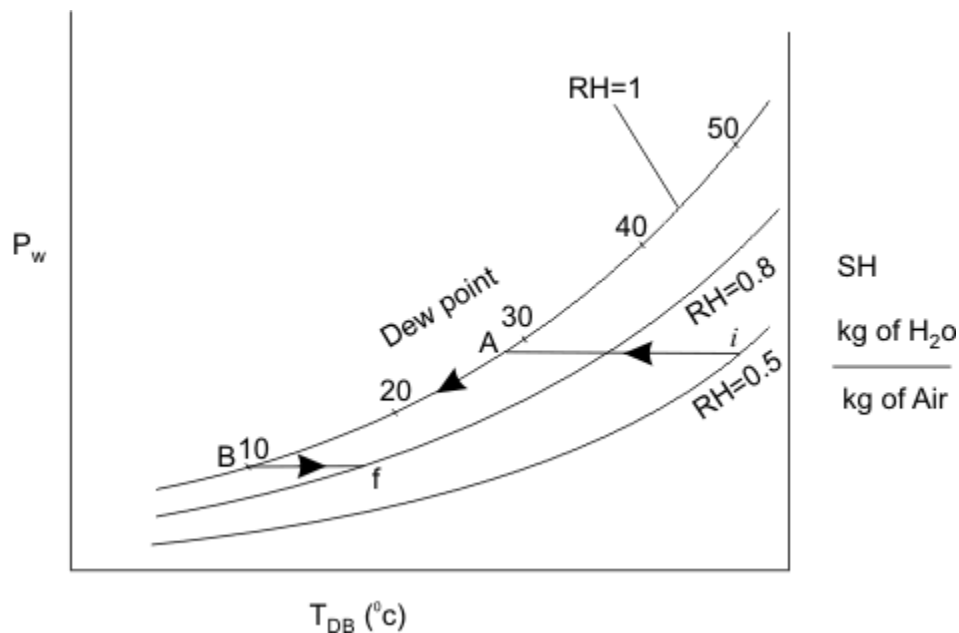
temperature T_{WB} lines run from the upper left to lower right of the chart. The relationship between the wet bulb temperature and other chart quantities are provided by using Eqn

$$w_1 = \frac{c_p (T_{WB} - T)_1 + w_2 h_{g2}}{h_{g1} - h_{f2}}$$

The lines of wet bulb temperature are approximately the lines of constant mixture enthalpy per unit mass of dry air.

Dehumidification:

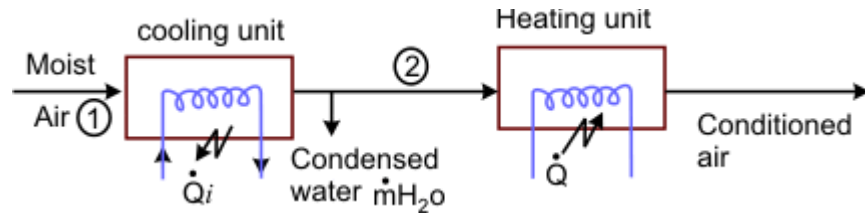
When a moist air steam is cooled at constant mixture pressure to a temperature below its dew point temperature, some condensation of water vapour would occur. Refer to figure 36.4 for understanding the process.



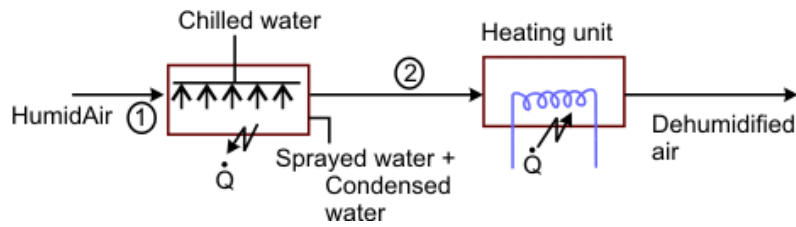
Dehumidification of air-water vapour mixture can be achieved by cooling the mixture below its dew point temperature (path i-A-B) allowing some water to condense, and then heating the mixture (path B-f) to the desired temperature.

Dehumidification and Cooling

For cooling the mixture, the mixture can be made to pass over the cooling coils through which a cold refrigerant is circulated

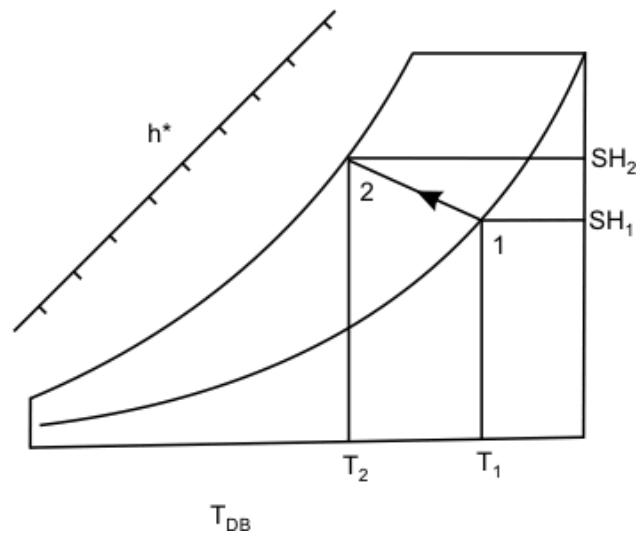


the mixture) is sprayed into the air to be dehumidified. Then the air leaves with less humidity at the temperature of the chilled water. Next the air is heated to the desired temperature

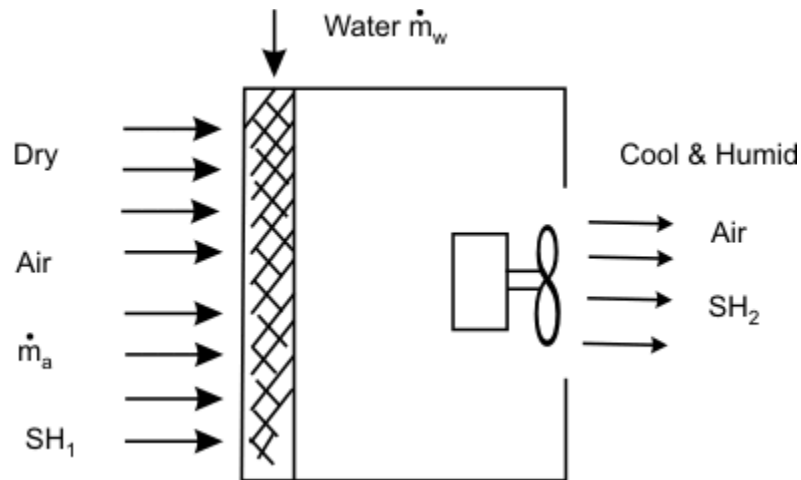


These two cooling and heating processes constitute an air conditioning plant.
Humidification with Cooling

The process is same as the Adiabatic saturation except that the air may leaves unsaturated.



Extensively used in desert coolers which is used for cooling homes in hot & dry climates. An unsaturated air-water vapour mixture is made to flow through porous pads soaked in water (figure 36.8)

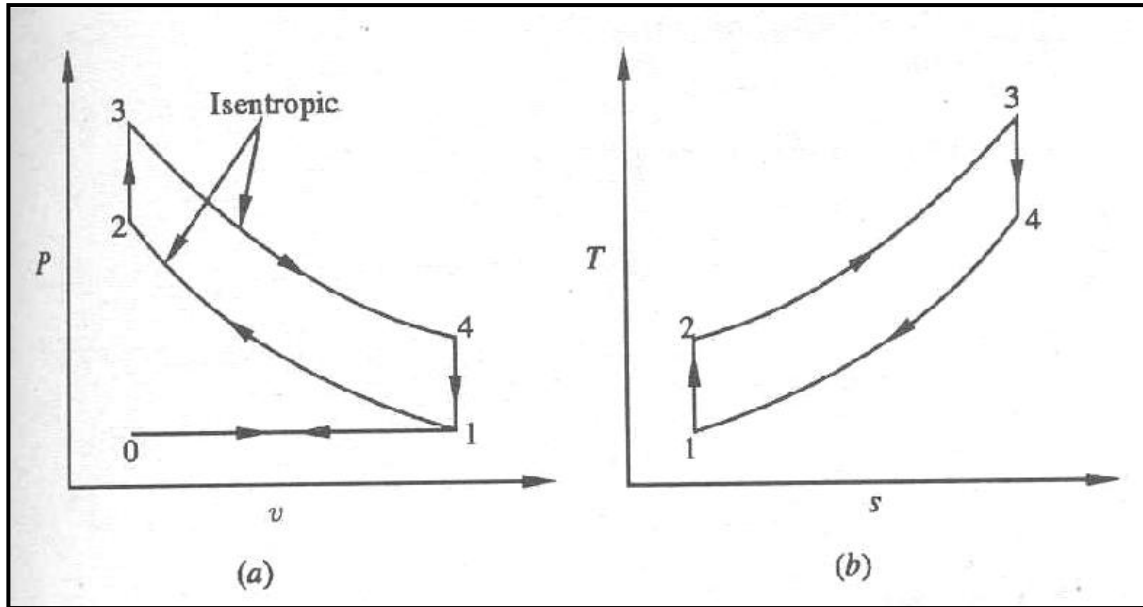


$$\dot{m}_w = \dot{m}_a (SH_2 - SH_1) = \dot{m}_a (w_2 - w_1)$$

\dot{m}_w denotes the rate at which water is evaporated. SH_1 and SH_2 are the specific humidity of air-water vapour mixture at the inlet and outlet respectively.

UNIT V POWER CYCLES

Air standard Otto Cycle



Air standard Otto cycle on (a) P-v diagram (b) T-s diagram

Processes: -

0-1: a fresh mixture of fuel-air is drawn into the cylinder at constant pressure

1-2: isentropic compression

2-3: energy addition at constant volume

3-4: isentropic expansion

4-1: combustion products leave the cylinder

1-0: the piston pushes out the remaining combustion products at constant pressure

Since the net work done in processes 0-1 and 1-0 is zero, for thermodynamic analysis, we consider the 1-2-3-4 only.

The thermal efficiency of the cycle is given by

$$\eta = \frac{W_{net}}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

where Q_1 and Q_2 denote the energy absorbed and rejected as heat respectively.

For a constant volume process $Q=\Delta U$. If 'm' is the mass of the air which is undergoing the cyclic process,

$$\Delta U = mC_v \Delta T$$

Energy is absorbed during the process 2-3

Energy is rejected during the process 4-1

Hence,

$$Q_1 = U_3 - U_2 = mC_v(T_3 - T_2)$$

$$Q_2 = U_4 - U_1 = mC_v(T_4 - T_1)$$

$$\therefore \eta = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

For an ideal gas undergoing an isentropic process (process 1-2 and 3-4),

$$TV^{\gamma-1} = \text{constant}$$

Hence,

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1} \right)^{\gamma-1}$$

$$\frac{T_4}{T_3} = \left(\frac{v_3}{v_4} \right)^{\gamma-1}$$

and

But $v_1=v_4$ and $v_2=v_3$. Hence we get,

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} \quad \text{or} \quad \frac{T_1}{T_4} = \frac{T_2}{T_3}$$

$$1 - \frac{T_1}{T_4} = 1 - \frac{T_2}{T_3} \quad \text{or} \quad \frac{T_4 - T_1}{T_4} = \frac{T_3 - T_2}{T_3}$$

$$\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3} = \frac{T_1}{T_2}$$

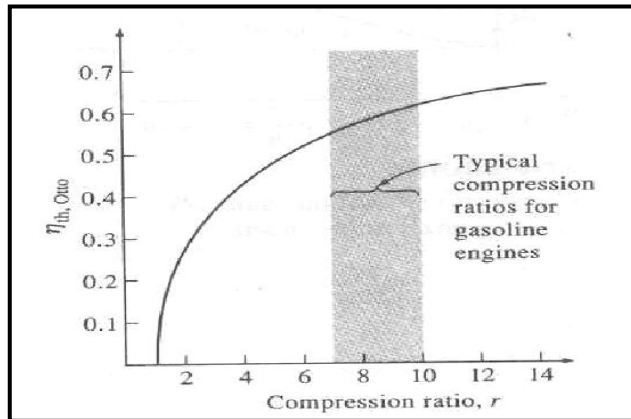
$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{v_2}{v_1} \right)^{\gamma-1} = 1 - \left(\frac{1}{r_0} \right)^{\gamma-1}$$

Hence,

Where the compression ratio r_0 is defined as

$$r_0 = \frac{v_1}{v_2}$$

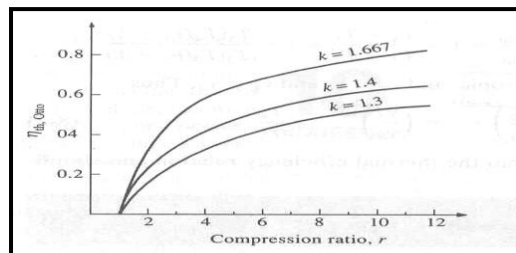
Sometimes it is convenient to express the performance of an engine in terms of *Mean effective Pressure*, P_m , defined as the ratio of Net work done” to “Displacement volume”



$$P_m = \frac{W}{v_1 - v_2}$$

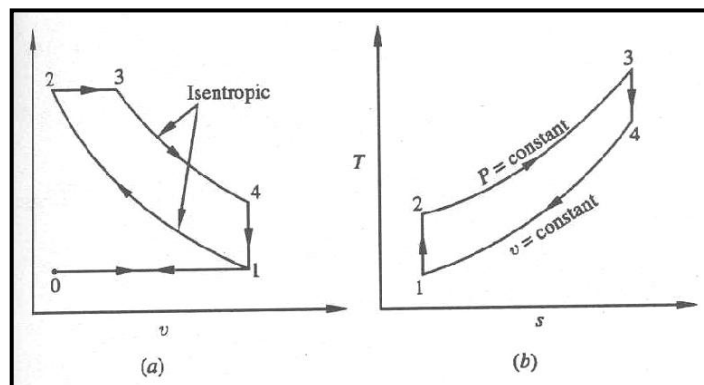
$$W = P_m (v_1 - v_2)$$

Thermal efficiency of the ideal Otto cycle as a function of compression ratio ($\gamma=1.4$)



The thermal efficiency of the Otto cycle increases with the specific heat ratio, γ of the working fluid.

Air standard Diesel cycle



Diesel cycle on (a) P-v diagram (b) T-s diagram

Processes: -

0-1: fresh air is drawn into the cylinder

1-2: isentropic compression

2-3: constant pressure energy addition

3-4: isentropic expansion

4-1: combustion products leave the cylinder

1-0: remaining combustion products are exhausted at constant pressure

Defining cutoff ratio, r_c as,

$$r_c = \frac{v_3}{v_2}$$

For a constant pressure process (2-3),

$$Q = \Delta H.$$

Hence, the energy addition during process 2-3,

$$Q_1 = H_3 - H_2 = m(h_3 - h_2) = mC_p(T_3 - T_2)$$

where 'm' is the mass of gas undergoing the cyclic change.

The energy rejection during the process 4-1,

$$Q_2 = U_4 - U_1 = m(u_4 - u_1) = mC_v(T_4 - T_1)$$

The thermal efficiency, η is given by

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{mC_p(T_3 - T_2) - mC_v(T_4 - T_1)}{mC_p(T_3 - T_2)}$$

$$\eta = 1 - \frac{T_4 - T_1}{\gamma(T_3 - T_2)} = 1 - \frac{T_1 \left(\frac{T_4}{T_1} - 1 \right)}{T_2 \gamma \left(\frac{T_3}{T_2} - 1 \right)}$$

Since the process 1-2 is isentropic,

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1} \right)^{\gamma-1} = \left(\frac{1}{r_0} \right)^{\gamma-1}$$

Since the process 4-1 is a constant volume process,

$$\frac{T_4}{T_1} = \frac{P_4}{P_1} = \frac{P_4}{P_3} \left(\frac{P_3}{P_1} \right) = \frac{P_4}{P_3} \left(\frac{P_2}{P_1} \right)$$

since $P_2 = P_3$

The processes 1-2 and 3-4 are isentropic. Hence,

$$\frac{P_4}{P_3} = \left(\frac{v_3}{v_4} \right)^{\gamma} \quad \text{and} \quad \frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^{\gamma}$$

Hence we get,

$$\frac{T_4}{T_1} = \left(\frac{v_3}{v_4} \right)^{\gamma} \left(\frac{v_1}{v_2} \right)^{\gamma} = \left(\frac{v_3}{v_2} \right)^{\gamma} = r_c^{\gamma}$$

For the constant pressure process,

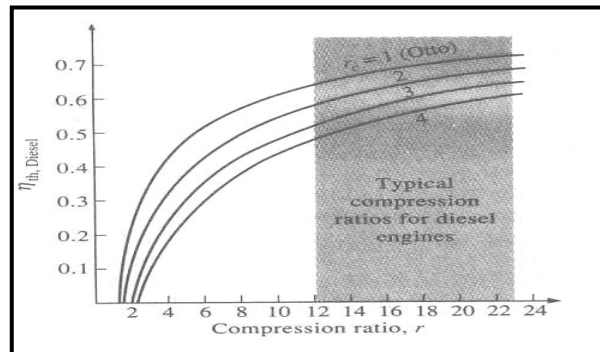
$$\frac{T_3}{T_2} = \frac{v_3}{v_2} = r_c$$

Hence the efficiency becomes,

$$\eta = 1 - \frac{1}{r_0^{\gamma-1}} \left[\frac{r_c^{\gamma} - 1}{r_c - 1} \right]$$

The mean effective pressure of an air standard diesel cycle is given by,

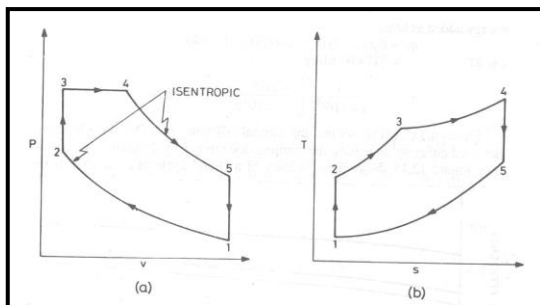
$$P_m = P_1 \frac{[\gamma_0^\gamma (r_c - 1) - r_0 (r_c^\gamma - 1)]}{(\gamma - 1)(r_0 - 1)}$$



Thermal efficiency of the ideal diesel cycle as a function of compression and cutoff ratios ($\gamma=1.4$)

Air standard Dual cycle

Dual cycle on (a) P-v diagram (b) T-s diagram



Energy addition is in two stages: Part of energy is added at constant volume and part of the energy is added at constant pressure

Energy added, q_1

$$q_1 = C_v(T_3 - T_2) + C_p(T_4 - T_3)$$

Energy rejected, q_2

$$q_2 = C_v(T_5 - T_1)$$

Thermal efficiency, η

$$\eta = 1 - \frac{q_2}{q_1}$$

$$\eta = 1 - \frac{C_v(T_5 - T_1)}{C_v(T_3 - T_2) + C_p(T_4 - T_3)}$$

$$\eta = 1 - \frac{(T_5 - T_1)}{(T_3 - T_2) + \gamma(T_4 - T_3)}$$

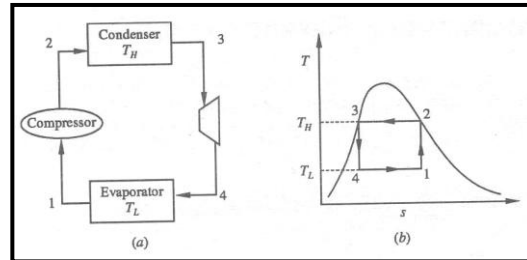
The efficiency can be expressed also in terms of,

Compression ratio, $r_0 = V_1/V_2$

Cut-off ratio, $r_c = V_4/V_3$

Constant volume pressure ratio, $r_{vp} = P_3/P_2$

Carnot Vapour compression Refrigeration cycle



(a) Schematic diagram

representation (b) T-s

Processes: -

1-2: Isentropic compression from state 1 (wet vapour) to state 2 (saturated vapour)

2-3: Heat rejection (Q_H) in the condenser

3-4: Isentropic expansion from state 3 (saturated liquid)

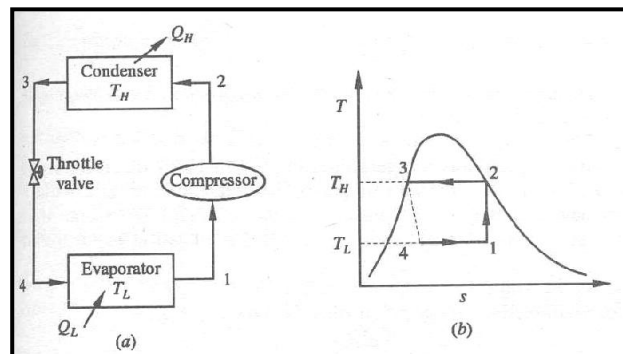
4-1: Heat absorption (Q_L) in the evaporator

The COP of the refrigerator,

$$(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L}$$

Practical Vapour compression refrigeration cycle

(a) schematic diagram (b) T-s diagram



Application of the first law of thermodynamics to the control volume compressor, condenser, throttle and evaporator gives

$$(W_s)_{\text{compressor}} = h_2 - h_1$$

$$Q_H = h_2 - h_3$$

$$h_3 = h_4$$

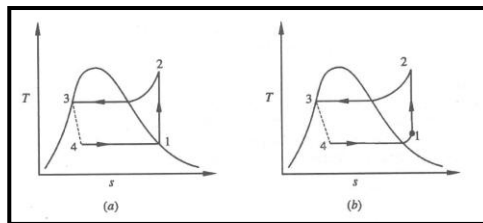
$$\text{and } Q_L = h_1 - h_4$$

The COP of the refrigerator is given by,

$$(COP)_R = \frac{Q_L}{W} = \frac{h_1 - h_4}{h_2 - h_1}$$

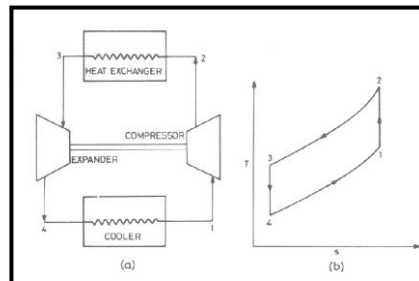
In the ideal refrigeration cycle, the refrigerant leaves the evaporator as wet vapour.

In some cases the refrigerant leaves the evaporator as either saturated vapour or superheated vapour.



T-s diagram for a vapour compression refrigeration cycle when the refrigerant leaves the evaporator as (a) saturated vapour (b) superheated vapour

Gas refrigeration cycle



(a) Schematic diagram (b) T-s diagram

The simplest gas refrigeration cycle is the reversed Brayton cycle

Processes: -

1-2: isentropic compression for state 1 (atmospheric air) to state 2

2-3: energy exchange with the surrounding, air is cooled

3-4: isentropic expansion to state 4

Work obtained during the expansion process can be used to run the compressor

Work done on the compressor,

$$W_c = h_2 - h_1 = C_p (T_2 - T_1)$$

Work delivered by the expander,

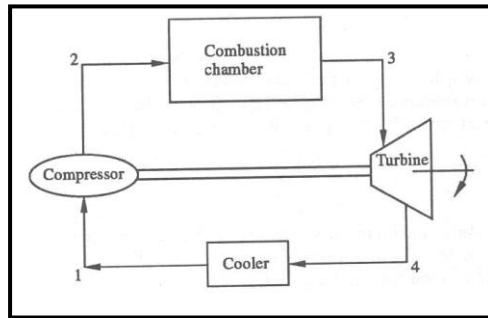
$$W_e = h_3 - h_4 = C_p (T_3 - T_4)$$

The net work required= $C_p (T_2 - T_1 - T_3 + T_4)$

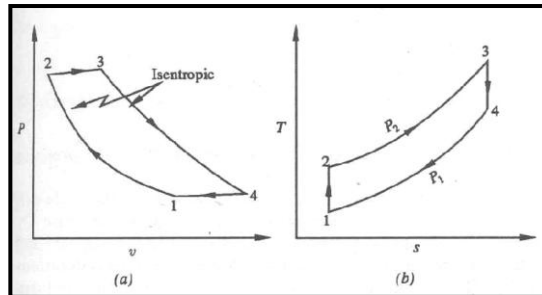
The COP of this refrigeration system is given by,

$$COP = \frac{Q_L}{W} = \frac{T_1 - T_4}{T_2 - T_1 - T_3 + T_4}$$

Air standard Brayton cycle



Schematic representation of an air standard Brayton cycle



Brayton cycle on (a) P-v diagram (b) T-s diagram

Processes: -

1-2: isentropic compression

2-3: constant pressure energy addition

3-4: isentropic expansion

4-1: constant pressure energy rejection

Energy added, $Q_1 = mC_p (T_3 - T_2)$

Energy rejected, $Q_2 = mC_p (T_4 - T_1)$

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

$$\eta = 1 - \frac{T_1 \left[\left(\frac{T_4}{T_1} \right) - 1 \right]}{T_2 \left[\left(\frac{T_3}{T_2} \right) - 1 \right]}$$

Thermal efficiency,

The pressure ratio of the Brayton cycle, r_p is defined as,

$$r_p = \frac{P_2}{P_1}$$

Then $\frac{P_3}{P_4} = \frac{P_2}{P_1}$

The processes 1-2 and 3-4 are isentropic. Hence,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

$$\frac{T_3}{T_4} = \left(\frac{P_3}{P_4} \right)^{\frac{\gamma-1}{\gamma}}$$

We get,

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} \quad \text{or} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2}$$

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}}$$

$$\eta = 1 - \left(\frac{1}{r_p} \right)^{\frac{\gamma-1}{\gamma}}$$

Work delivered by the cycle is given by $W = \eta Q_1$

Increasing Q_1 can increase work done by the cycle

Since the Turbine blade material cannot withstand very high temperature, T_3 and hence Q_1 is limited

The optimum pressure ratio for fixed values of T_1 and T_3 , for which work is maximum, is obtained by,

$$W_{net} = Q_1 - Q_2 = mC_p(T_3 - T_2) - mC_p(T_4 - T_1)$$

$$W_{net} = mC_p[(T_3 - T_4) - (T_2 - T_1)]$$

$$W_{net} = mC_p \left[T_3 \left(1 - \frac{T_4}{T_3} \right) - T_1 \left(\frac{T_2}{T_1} - 1 \right) \right]$$

$$W_{net} = mC_p \left[T_3 \left(1 - \left(\frac{1}{r_p} \right)^{\frac{\gamma-1}{\gamma}} \right) - T_1 \left((r_p)^{\frac{\gamma-1}{\gamma}} - 1 \right) \right]$$

For optimum pressure ratio,

$$\frac{dW_{net}}{dr_p} = mC_p T_3 \left(\frac{\gamma-1}{\gamma} \right) (r_p)^{\left(\frac{1-2\gamma}{\gamma} \right)} -$$

$$mC_p T_1 \left(\frac{\gamma-1}{\gamma} \right) (r_p)^{-\frac{1}{\gamma}} = 0$$

$$T_3 (r_p)^{\left(\frac{1-2\gamma}{\gamma} \right)} =$$

$$\text{or} \quad T_1 (r_p)^{-\frac{1}{\gamma}}$$

$$\text{or} \quad \frac{T_3}{T_1} = (r_p)^{\frac{2(\gamma-1)}{\gamma}}$$

$$\text{or} \quad r_p = \left(\frac{T_3}{T_1} \right)^{\frac{\gamma}{2(\gamma-1)}}$$

COMPARISON OF OTTO, DIESEL AND DUAL CYCLE

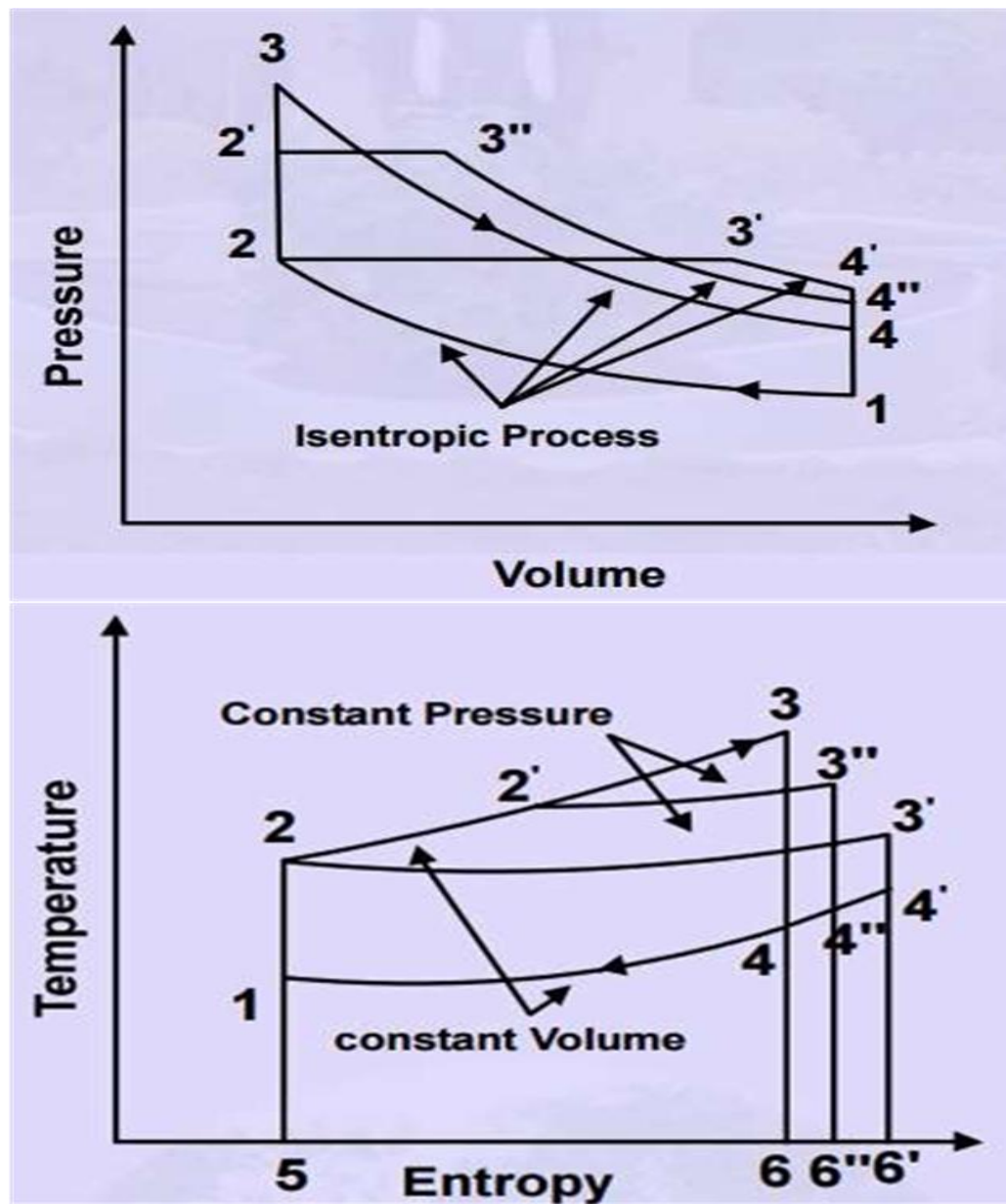
- Following are the important variable factors which are used for comparison of these cycles:

1. Compression ratio
2. Maximum pressure
3. Heat supplied
4. Heat rejected and Net work

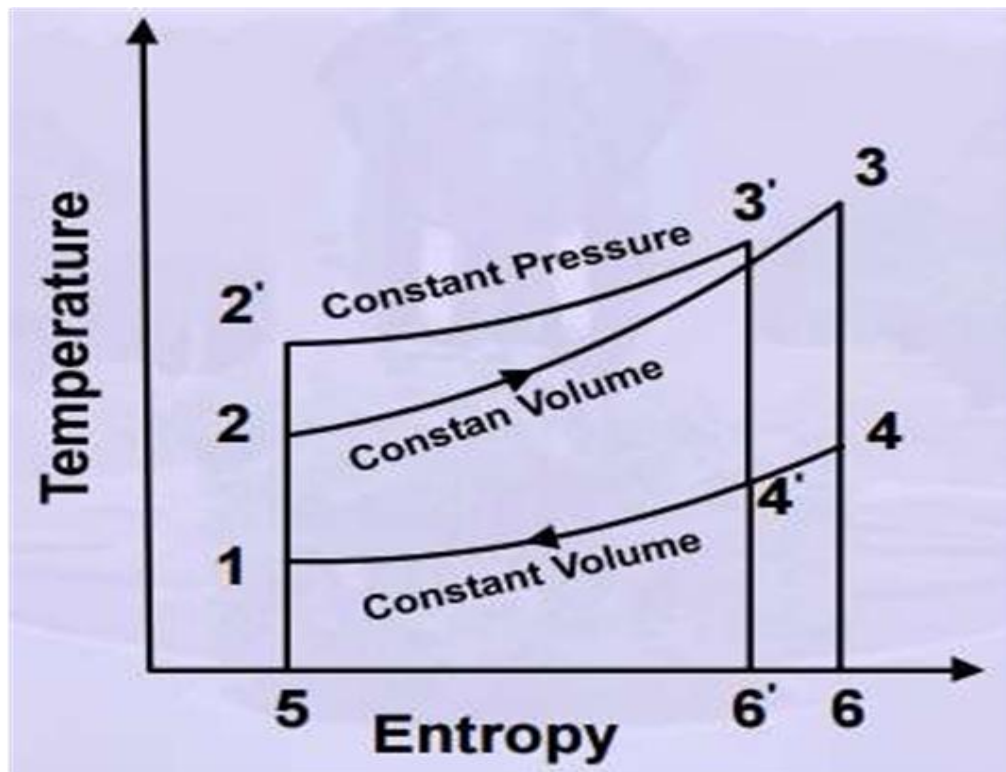
Efficiency versus compression ratio

For a given compression ratio, Otto cycle is the most efficient while the diesel cycle is the least efficient

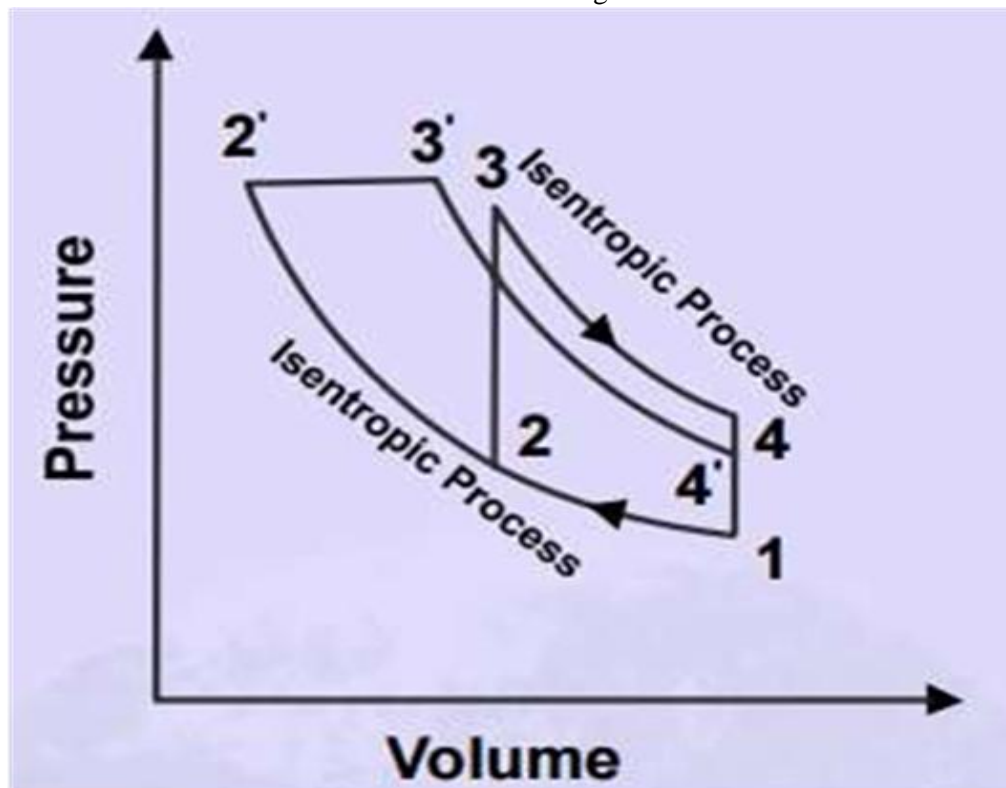
For the same compression ratio and the same heat input



For constant maximum pressure and heat supplied



T-S diagram



P-V DIAGRAM