ENGINEERING THERMODYNAMICS

UNIT I

Introductory Concepts.

Definition of THERMODYNAMICS:

- Thermodynamics is the science that includes the study of energy transformations and of the relationships among the physical properties of the substances which are affected by these transformations.

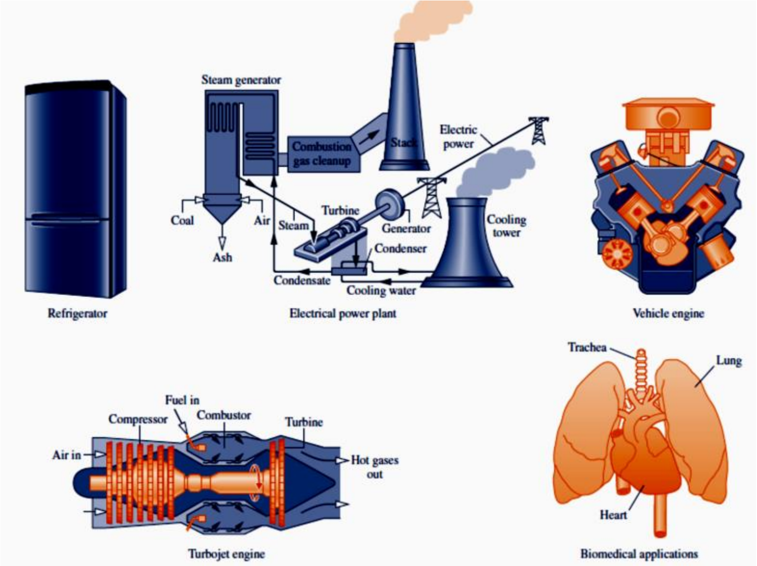
- The term 'Thermodynamics' was first used in a publication by Lord Kelvin in 1849. The first thermodynamics textbook was written in 1859 by William Rankine, a professor at the University of Glasgow.

- **Scope of Thermodynamics**

Although aspects of thermodynamics have been studied since ancient times, the formal study of thermodynamics began in the early nineteenth century through consideration of the capacity of hot objects to produce work. Today the scope is much larger. Thermodynamics now provides essential concepts and methods for addressing critical twenty-first-century issues, such as using fossil fuels more effectively, fostering renewable energy technologies, and developing more fuel-efficient means of transportation. Also critical are the related issues of greenhouse gas emissions and air and water pollution. Thermodynamics is both a branch of science and an engineering specialty. Engineers are generally interested in studying systems and how they interact with their surroundings. To facilitate this, thermodynamics has been extended to the study of systems through which matter flows, including bioengineering and biomedical systems.

Areas of Application of Engineering Thermodynamics

1. Aircraft and rocket propulsion,
2. Alternative energy systems
3. Fuel cells
4. Geothermal systems
5. Wind turbines
6. Automobile engines
7. Bioengineering applications
8. Biomedical applications
9. Combustion systems
10. Compressors, pumps
11. Steam and gas turbines
12. Power production
13. Propulsion
14. Magneto hydrodynamic (MHD) converters
15. Ocean thermal, wave, and tidal power generation
16. Solar-activated heating, cooling, and power generation
17. Thermoelectric and thermionic devices
18. Cooling of electronic equipment
19. Cryogenic systems, gas separation, and liquefaction



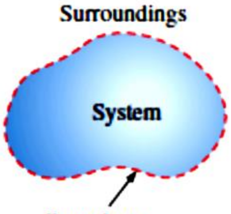
20. Fossil and nuclear-fuelled power stations
21. Heating, ventilating, and air-conditioning systems
22. Absorption refrigeration and heat pumps
23. Vapour-compression refrigeration and heat pumps

Thermodynamic Properties and energy relationships can be studied by two methods.
(i) Classical Thermodynamics
(ii) Statistical Thermodynamics

i. **Classical and statistical Thermodynamics:** It Involve studies which are undertaken without recourse to the nature of the Individual Particles which make up a substance and to their reactions. This is macroscopic view towards matter, and it requires no hypothesis about the detailed structure of matter on the atomic scale.
For **example**, the pressure of a gas in a container is the result of momentum transfer between the molecules and the walls of the container. However, one does not need to know the behaviour of the gas particles to determine the pressure in the container. It would be sufficient to attach a pressure gage to the container.
classical thermodynamics allows important aspects of system behaviour to be evaluated from observations of the overall system. It provides a direct and easy way to the solution of engineering problems.

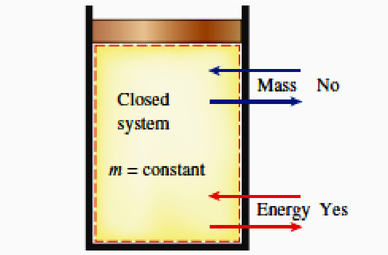
ii. **Statistical Thermodynamics:** It is based on the statistical behaviour of large groups of Individual particles. This is microscopic view point of matter.
The statistical thermodynamics or microscopic approach to thermodynamics, is concerned directly with the structure of matter. The objective of statistical thermodynamics is to characterize by statistical means the average behaviour of the particles making up a system of interest and relate this information to the observed macroscopic behaviour of the system.
For applications involving lasers, plasmas, high speed gas flows, chemical kinetics, very low temperatures (cryogenics), and others, the methods of statistical thermodynamics are essential.

System: A thermodynamic system is a Three dimensional region of space or an amount of matter, bounded by an arbitrary surface.
Everything external to the system is considered to be part of the system's **surroundings**. The system is distinguished from its surroundings by a specified **boundary**, which may be at rest or in motion.

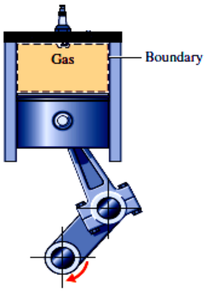


Systems may be considered to be *closed* or *open*, depending on whether a fixed mass or a fixed volume in space is chosen for study. A **closed system** (also known as a **control mass** or just *system* when the context makes it clear) consists of a fixed amount of mass, and no mass can cross its boundary. That is, no mass can enter or leave a closed system, as shown in fig. However energy may cross the system boundary.

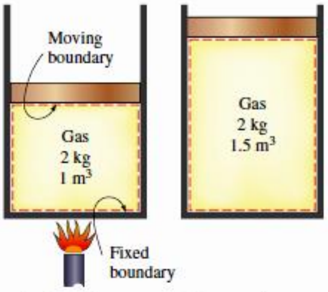
Examples:



Mass cannot cross the boundaries of a closed system, but energy can.



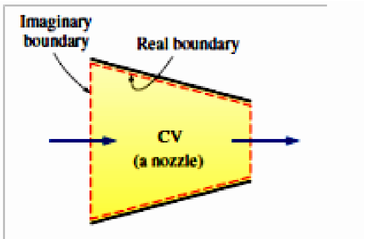
Closed system: A gas in a piston–cylinder assembly.



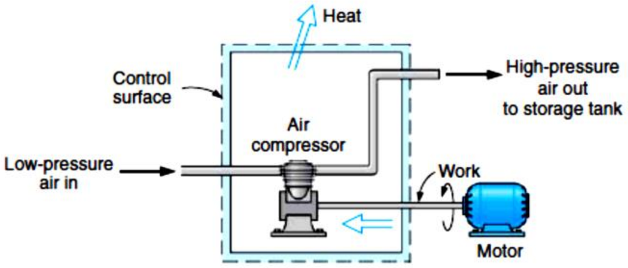
A closed system with a moving boundary.

An **open system**, or a **control volume**, as it is often called, is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor, turbine, or nozzle. Flow through these devices is best studied by selecting the region within the device as the control volume. Both mass and energy can cross the boundary of a control volume. The boundaries of a control volume are called a *control surface,* and they can be real or imaginary.

A large number of engineering problems involve mass flow in and out of a system and, therefore, are modelled as *control volumes.*
Example: A water heater, a car radiator, a turbine, and a compressor all involve mass flow and should be analyzed as control volumes (open systems) instead of as control masses (closed systems).



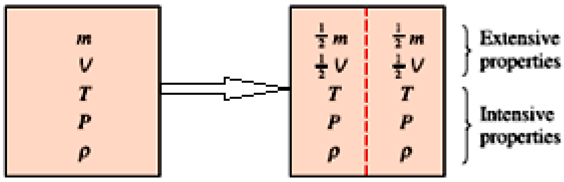
A control volume (CV) with real and imaginary boundaries



- **Properties:** The state or physical condition of the system can be described by some parameters called as Properties. Properties are the coordinates to describe the state of the system. Every property has a fixed value at a particular state.
  Some familiar properties are pressure P, temperature T, volume V, and mass m. The list can be extended to include less familiar ones such as viscosity, thermal conductivity, modulus of elasticity, thermal expansion coefficient, electric resistivity, and even velocity and elevation.

- Properties are considered to be either *intensive* or *extensive*.
- **Intensive properties** are those that are independent of the Size or Extent or mass of a system, such as temperature, pressure, and density.
- **Extensive properties** are those whose values depend on the size—or extent—of the system. Total mass, total volume, and total momentum are some examples of extensive properties. An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with an imaginary partition, as shown in Fig. Each part will have the same

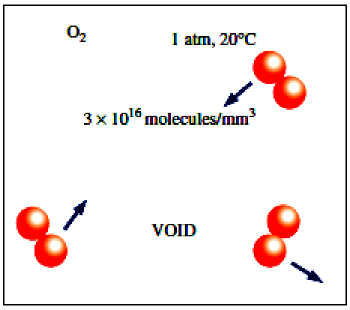
value of intensive properties as the original system, but half the value of the extensive properties.



Criterion to differentiate intensive and extensive properties.

- Extensive properties per unit mass are called **specific properties**. Some examples of specific properties are specific volume ($v = V/m$) and specific total energy ($e = E/m$).
- **Continuum:** Matter is made up of atoms that are widely spaced in the gas phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a continuous, homogeneous matter with no holes, that is, a **continuum**.
- The continuum idealization allows us to treat properties as point functions and to assume the properties vary continually in space with no jump discontinuities. This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules.

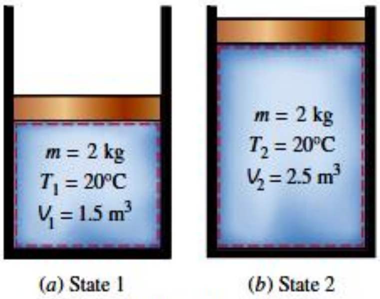
- To have a sense of the distance involved at the molecular level, consider a container filled with oxygen at atmospheric conditions. The diameter of the oxygen molecule is about
- 3 x10^{-10} m and its mass is 5.3 x 10^{-26} kg. Also, the *mean free path* of oxygen at 1 atm pressure and 20°C is 6.3 x 10^{28} m. That is, an oxygen molecule travels, on average, a distance of 6.3 X 10^{28} m (about 200 times of its diameter) before it collides with another molecule.
- Also, there are about 3 X 10^{16} molecules of oxygen in the tiny volume of 1 mm^3 at 1 atm pressure and 20°C. The continuum model is applicable as long as the characteristic length of the system (such as its diameter) is much larger than the mean free path of the molecules.
- At very high vacuums or very high elevations, the mean free path may become large (for example, it is about 0.1 m for atmospheric air at an elevation of 100 km). For such cases the **rarefied gas flow theory** should be used, and the impact of individual molecules should be considered. In this text we will limit our consideration to substances that can be modelled as a continuum.



Despite the relatively large gaps between molecules, a gas can usually be treated as a continuum because of the very large number of molecules even in an extremely small volume.

- **State:** The state of a system is the condition of the system described by the values of its properties.
- **Equilibrium:** If the Properties are invariant with respect to time then that state is called as an Equilibrium state.

Consider a system not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition, or the **state**, of the system. At a given state, all the properties of a system have fixed values. If the value of even one property changes, the state will change to a different one. In the below figure shows a system at two different states.



(*a*) State 1 (*b*) State 2

A system at two different states.

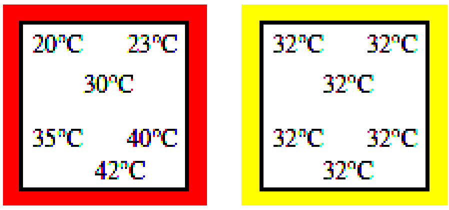
There are many types of equilibrium, and a system is not in **thermodynamic equilibrium** unless the conditions of all the relevant types of equilibrium are satisfied. For example,

iii. a system is in **thermal equilibrium** if the temperature is the same throughout the entire system, as shown in Fig. That is, the system involves no temperature differential, which is the driving force for heat flow.

iv. **Mechanical equilibrium** is related to pressure, and a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time. However, the pressure may vary within the system with elevation as a result of gravitational effects.

v. Finally, a system is in **chemical equilibrium** if its chemical composition does not change with time, that is, no chemical reactions occur. A system will not be in equilibrium unless all the relevant equilibrium criteria are satisfied.

If all the above equilibrium are satisfied then the system is said to be in Thermodynamic Equilibrium.



(*a*) Before (*b*) After

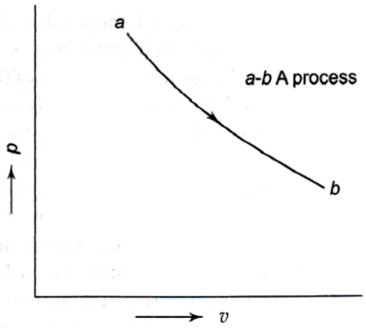
A closed system reaching thermal equilibrium.

State Postulate:

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

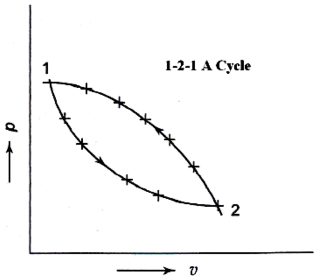
Processes and cycles:

- ➢ Any change that a system undergoes from one equilibrium state to another is called a **process**, and the series of states through which a system passes during a process is called the **path** of the process.



- To describe a process completely, one should specify the initial and final states of the process, as well as the path it follows, and the interactions with the surroundings.

If the process proceeds in such a way that if the final state is same as initial state then a **CYCLE** is said to be completed.



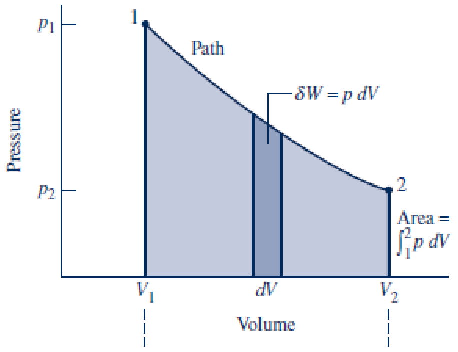
- **Quasi static Process**

  When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a **quasi-static**, or **quasi-equilibrium**, **process**.

- **Expansion or Compression Work in Quasi-Equilibrium Processes**

A Quasi Equilibrium process is one in which the departure from thermodynamic equilibrium is at most infinitesimal. All states through which the system passes in a quasi equilibrium process may be considered equilibrium states. Because non equilibrium effects are inevitably present during actual processes, systems of engineering interest can at best approach, but never realize, a quasi equilibrium process.

Imagine that one of the masses is removed, allowing the piston to move upward as the gas expands slightly. During such an expansion, the state of the gas would depart only slightly from equilibrium. The system would eventually come to a new equilibrium state, where the pressure and all other intensive properties would again be uniform in value. Moreover, were the mass replaced, the gas would be restored to its initial state, while again the departure from equilibrium would be slight. If several of the masses were removed one after another, the gas would pass through a sequence of equilibrium states without ever being far from equilibrium. In the limit as the increments of mass are made vanishingly small, the gas would undergo a quasi equilibrium expansion process. A quasi equilibrium compression can be visualized with similar considerations.



Work of a quasiequilibrium expansion or compression process.

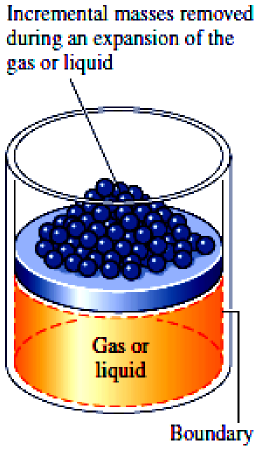


Illustration of a quasiequilibrium expansion or compression.

TEMPERATURE AND THE ZEROTH LAW OF THERMODYNAMICS

Temperature is rooted in the notion of the “hotness” or “coldness” of objects. We use our sense of touch to distinguish hot objects from cold objects and to arrange objects in their order of “hotness,” deciding that 1 is hotter than 2, 2 hotter than 3, and so on. But however sensitive human touch may be, we are unable to gauge this quality precisely.

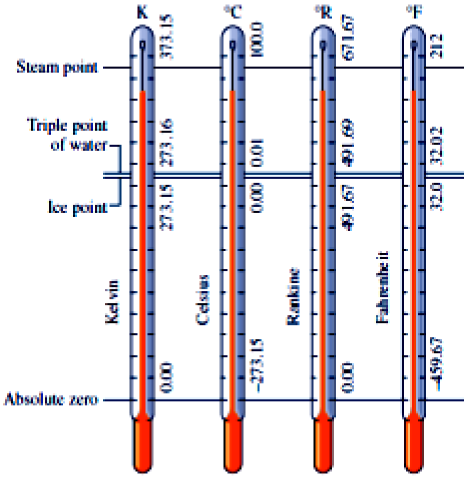
To illustrate this, consider two copper blocks, and suppose that our senses tell us that one is warmer than the other. If the blocks were brought into contact and isolated from their surroundings, they would interact in a way that can be described as a **thermal (heat) interaction**. During this interaction, it would be observed that the volume of the warmer block decreases somewhat with time, while the volume of the colder block increases with time. Eventually, no further changes in volume would be observed, and the blocks would feel equally warm. Similarly, we would be able to observe that the electrical resistance of the warmer block decreases with time and that of the colder block increases with time; eventually the electrical resistances would become constant also. When all changes in such observable properties cease, the interaction is at an end. The two blocks are then in **thermal equilibrium**. Considerations such as these lead us to infer that the blocks have a physical property that determines whether they will be in thermal equilibrium. This property is called **temperature**, and we postulate that when the two blocks are in thermal equilibrium, their temperatures are equal.

Zeroth Law of Thermodynamics:

- when two objects are in thermal equilibrium with a third object, they are in thermal equilibrium with one another.
- If we want to know if two objects are at the same temperature, it is not necessary to bring them into contact and see whether their observable properties change with time, as described previously. It is necessary only to see if they are individually in thermal equilibrium with a third object. The third object is usually a *thermometer*.
- Any object with at least one measurable property that changes as its temperature changes can be used as a thermometer. Such a property is called a **thermometric property**. The particular substance that exhibits changes in the thermometric property is known as a *thermometric substance*.

Temperature scales:

- The temperature scales used in the SI and in the English system today are the **Celsius scale** and the **Fahrenheit scale** respectively**.** On the Celsius scale, the ice and steam points were originally assigned the values of 0 and 100°C, respectively. The corresponding values on the Fahrenheit scale are 32 and 212°F. These are often referred to as *two-point scales* since temperature values are assigned at two different points.
- In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of any substance or substances. Such a temperature scale is called a **thermodynamic temperature scale**, which is developed later in conjunction with the second law of thermodynamics.
- The thermodynamic temperature scale in the SI is the **Kelvin scale**, named after Lord Kelvin (1824–1907). The temperature unit on this scale is the **kelvin**, which is designated by K. The lowest temperature on the Kelvin scale is absolute zero, or 0 K.
- The thermodynamic temperature scale in the English system is the **Rankine scale**, named after William Rankine (1820–1872). The temperature unit on this scale is the **rankine**, which is designated by R.
- The relationship of the Kelvin, Rankine, Celsius, and Fahrenheit scales is shown in Fig. together with values for temperature at three fixed points: the triple point, ice point, and steam point.
- By international agreement, temperature scales are defined by the numerical value assigned to the easily reproducible **triple point** of water: the state of equilibrium among steam, ice and liquid water. The temperature at this standard fixed point is defined as 273.16 Kelvins, abbreviated as 273.16 K.



Comparison of temperature scales.

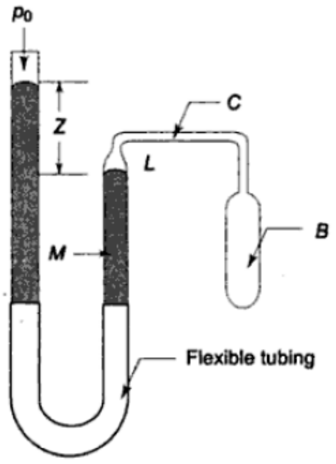
- The relationship between centigrade scale and Kelvin scale is T(^{0}C)= T(K) -273.15.
- The relationship between fahrenheit scale and Rankine scale is T(^{0}F)= T(R) -459.67.
- The relationship between fahrenheit scale and centigrade scale is T(^{0}F)= 1.8T(^{0}C) +32

Constant volume Gas thermometer:

- A small amount of gas is enclosed in bulb B which is in communication via the capillary tube C with one limb of the mercury manometer M. The other limb of mercury manometer is open to the atmosphere and can be moved vertically to adjust the mercury levels so that mercury just touches the Lip L of the capillary. The pressure in the bulb is used as a thermometric property and is given by

$p = p_o + \rho_m Zg.$

where p_o is the atmospheric pressure and ρ_m is the density of mercury.



Constant volume gas thermometer

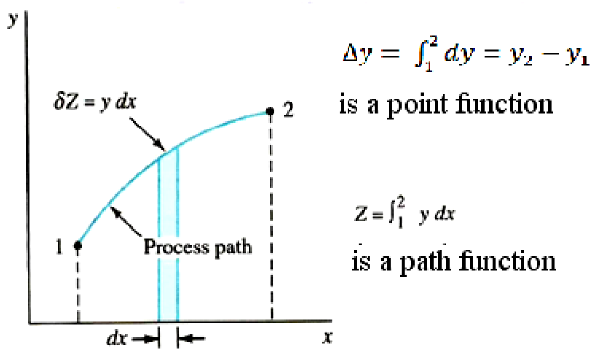
when the bulb is brought in contact with the system whose temperature is to be measured, the bulb, in course of time, comes in thermal equilibrium with the system. The gas in the bulb expands, on being heated, pushing the mercury downwards. The flexible limb of the manometer is then adjusted so that the mercury again touches the lip L. The difference in the mercury levels Z is recorded and the pressure p of the gas in the bulb is estimated. since the volume of the trapped gas remains constant, from the ideal gas equation

$$\Delta T = \frac{V}{R}\Delta P$$

i.e temperature increase is proportional to pressure increase.

Point and Path functions:

- Thermodynamic quantities can be divided into two categories: point or state functions and path or process functions.



- All properties are state functions, since the change in the value of a property depends solely on the property values at the initial and final states, and not on the path of the process.
- A property change for a process with given end states 1 and 2 is described mathematically by the exact differential *dy*, such that

$$\Delta y = \int_1^2 dy$$

- Quantities whose values depend on the path of the process are called process or path functions.
- Path functions are inexact differentials and hence

$$Z_{12} \neq \int_1^2 dz$$

The two major process functions in thermodynamic studies are work and heat.

Density, Specific Volume, and Specific Gravity:

- The density ρ is defined as the mass per unit volume:

$\rho = \frac{mass}{volume} = \frac{m}{v}$,its unit is kg per m^3

- The specific volume v is defined as volume per unit mass:

$v = \frac{volume}{mass} = \frac{V}{m}$, its unit is m^3 per kg

- The specific gravity of a substance is the ratio of its density to that of water at a specified temperature, such as 4 or 20^oC and one atmosphere:

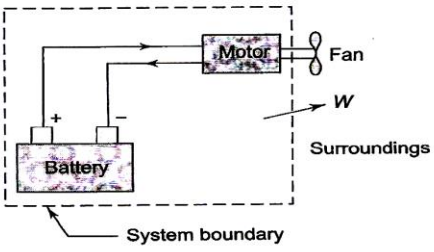
$$Sp.gr = \frac{\rho}{\rho_{water}} \text{ it has no units}$$

- The density of water at 4^oC is close to 1.00 g/cm^3 (kg/L), 1000 kg/m^3, while that of liquid mercury is close to 13.6 g/cm^3, 13600 kg/m^3.
- The specific weight *w* of a substance is the weight per unit volume:

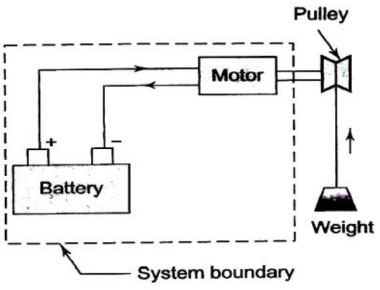
$w = \frac{weight}{volume} = \frac{W}{V}$, its unit is N per m^3

Thermodynamic work

- Work is said to be done by a system if the sole effect on things external to the system can be reduced to the raising of a weight.



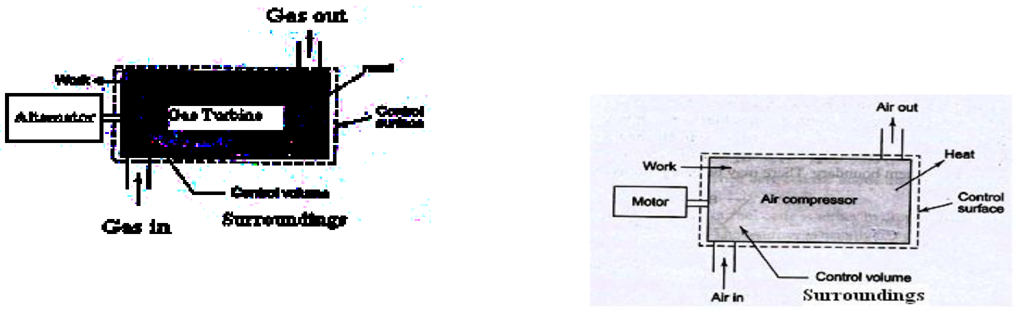
Battery-motor System driving a fan



Work transfer from a System

Sign Convention:

- When work is done by a system it is arbitrarily taken to be positive, and when work is done on a system, it is taken to be negative.



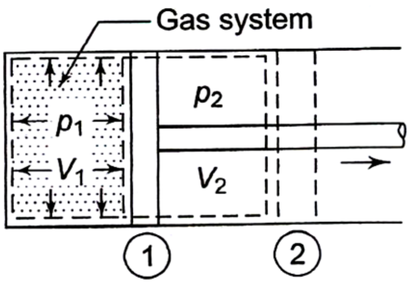
(a) W is positive (b) W is negative

Work interaction between a System and the Surroundings

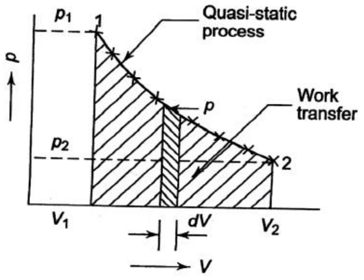
- The symbol W is used for work transfer. The unit of work is N.m or Joule.
- The rate at which the work is done by, or upon, the system is known as power. The unit of power is J/s or Watt.

Displacement work or pdV Work:

- Consider expansion of gas in a piston-cylinder assembly as shown in fig. 1.13.
- The expansion of the gas by outward movement of the piston can be represented on p-V diagram as given in Fig.1.14.



pdV work



Quasi-static pdV work

- The shaded area represents work done due to small movement of the piston and the total work done by the gas during expansion process is

$$W_{1-2} = \int_1^2 pdV$$

- The integral $\int_1^2 pdV$ can be evaluated, only if we know the relation between p and V or the path of the process.
- The area under the curve 1-2 represents the work done during the process 1-2.

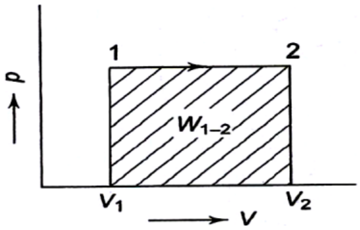
pdV-work in Various Quasi-Static Processes:

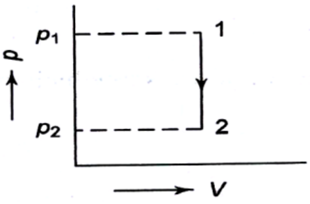
- Constant pressure process (isobaric or isopiestic process)

$$W_{1-2} = \int_1^2 pdV = p(V_2 - V_1)$$

- Constant volume process (isochoric process)

$$2W_{1-2} = \int_1^2 pdV = 0$$





Constant Pressure Process **Constant Volume Process**

- Process in which pV = C

$$W_{1-2} = \int_{V1}^{V2} pdV = p_1v_1 ln\frac{V_2}{V_1} = p_1v_1 ln\frac{P_1}{P_2}$$

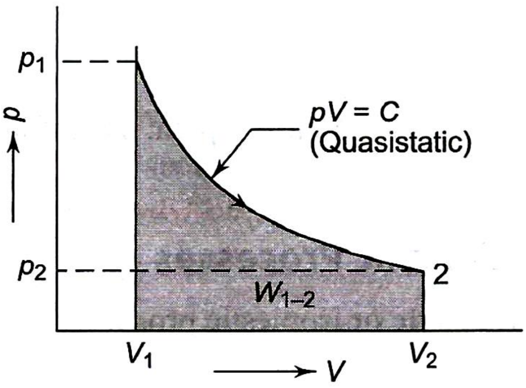
- Process in which pV^n=C, where n is a constant

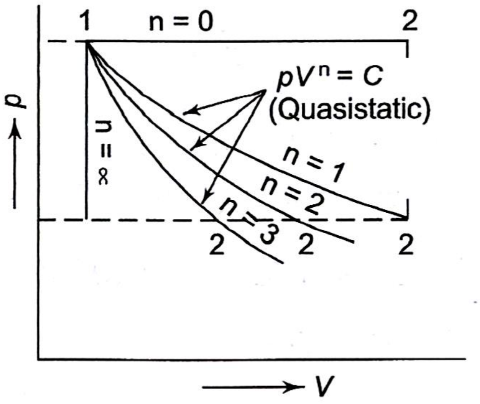
  $p_1{v_1}^n = p_2{v_2}^n$

  $p = \frac{p_1{v_1}^n}{v^n}$

$$W_{1-2} = \int_{V_1}^{V_2} \frac{C}{v^n} dv = C\left[\frac{V_2^{1-n}}{1-n} - \frac{V_1^{1-n}}{1-n}\right] = p_2{v_2}^n * \frac{V_2^{1-n}}{1-n} - p_1{v_1}^n * \frac{V_1^{1-n}}{1-n}$$

$$\therefore W_{1-2} = \frac{p_2v_2 - p_1v_1}{n-1}$$





Process in which pV=Constant **Profess in which pV^n=Constant**

Similarly, for process in which pv^γ=C

$$W_{1-2} = \frac{p_2v_2 - p_1v_1}{\gamma - 1}$$

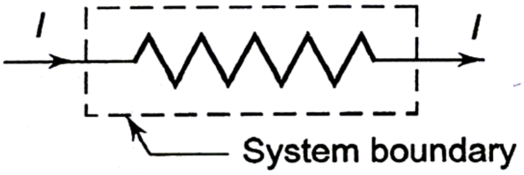
Other Types of Work Transfer

Electrical Work:

- When a current flows through a resistor, taken as a system, there is work transfer into the system.
- It is a thermodynamic work because the current can drive a motor, the motor can drive a pulley and the pulley can raise a weight.
- The current flow, *I*, in amperes, is given as

$I = \frac{dc}{dt}$ where C is the charge in coulombs and *t* is time in seconds.

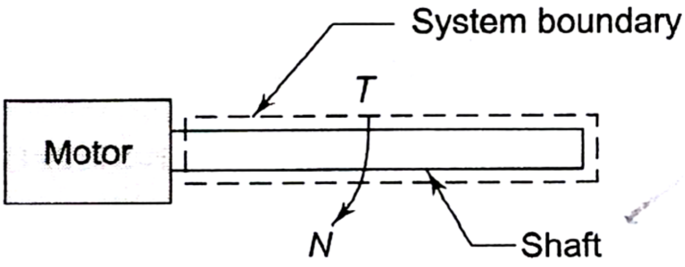
- If E is the voltage potential, the work, $dW = E.dc = EIdt$
- $W = E.dc = \int_{t_1}^{t_2} EIdt$



Electrical Work

Shaft Work:

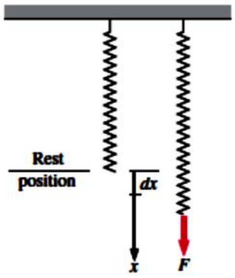
- When a shaft rotated by a motor, taken as a system, there is work transfer into the system.



Shaft work

- This is a form of thermodynamic work because the shaft can rotate a pulley which can raise a weight.
- If T is the torque applied to the shaft and $d\theta$ is the angular displacement of the shaft, the shaft work is $W = \int_1^2 Td\theta$

Spring Work:



- It is common knowledge that when a force is applied on a spring, the length of the spring changes.
- When the length of the spring changes by a differential amount *dx* under the influence of a force *F*, the work done is

$$dW_{spring} = F\,dx$$

- The displacement x is proportional to the force applied

$$F = kx \qquad (kN)$$

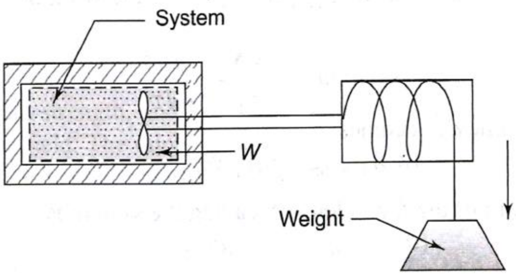
- where k is the spring constant and has the unit kN/m. The displacement *x* is measured from the undisturbed position of the spring (that is, *x* = 0 when F = 0).
- Work done = F.distance

For Infinitesimal extension (dx) of spring work is $\delta w = F.dx$

$$\text{Total } work = \int_1^2 Fdx = \int_1^2 kxdx = k\left[\frac{x_2^2}{2} - \frac{x_1^2}{2}\right] \qquad \text{(kJ)}$$

where x_1 and x_2 are the initial and the final displacements of the spring, respectively, measured from the undisturbed position of the spring.

Paddle-wheel work or Stirring Work:



- The paddle-wheel turns when the weight is lowered.
- The paddle-wheel stirs fluid system and hence, there is work transfer into the fluid system.
- Since the volume of the system remains constant, $\int_1^2 \mathrm{pdV} = 0$
- If m is the mass of the weight lowered through a distance dz and T is the torque transmitted by the shaft in rotating through an angle dθ , the differential work transfer to the fluid is given by

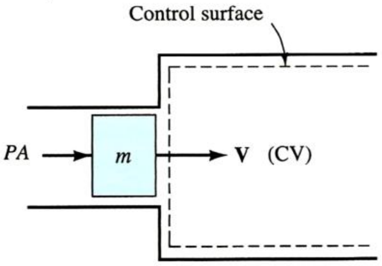
  dW = mgdz = $Td\theta$ =$W = \int_1^2 mgdz = \int_1^2 Td\theta = 0$

- The total work transfer is

$$mg\Delta z = T\Delta\theta$$

Flow Work:

- The flow work is significant only in a flow process or an open system.
- When mass *m* enters or leaves a control volume, work is required to push the fluid into or out of the system. This term is referred to as flow work.
- A mass *m* in region *A* (Fig. 1.21) initially resides just outside a control surface.



Flow work at a Control Surface

- The normal force exerted at the control surface of area *A* is simply the pressure times the area, or *PA*.
- Thus the rate of flow work $\dot{W}_{flow}$ is given by

  $\dot{W}_{flow}$ =pAV, where V is the velocity of fluid mass *m*.

  Since *m* = AV/v, therefore $\dot{W}_{flow} = pmv$. Where *v* is the specific volume.

- The flow work per unit mass is pv.

Work done in Stretching a Wire:

- Let us consider a wire as the system.
- If the length of the wire is changed from L to L + dL, the infinitestimal amount of work that is done is equal to dW = - F dL, where F is the tension in the wire.

- The minus sign is used because a positive value of dL means an expansion of the wire, for which work must be done on the wire, i.e., negative work.

- For a finite change of length.

  $W = -\int_1^2 Fdl$

- If we limit the problem to within the elastic limit, where E is the modulus of elasticity, τ is the stress, ε is the strain, and A is the cross-sectional area, then

$$F = \tau A = E\epsilon A, since\ E = \frac{\tau}{\varepsilon}$$

and $= \frac{dl}{L}$.

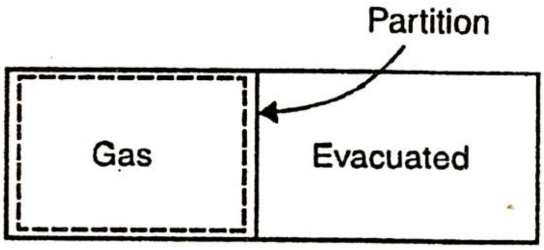
$$dw = -FdL = -E\epsilon ALd\varepsilon$$

$$\therefore W = -A\varepsilon L\int_1^2 \epsilon d\epsilon = -\frac{AEL}{2(\epsilon_2^2 - \varepsilon_1^2)}$$

Unrestrained or Free Expansion:

- The expansion of gas against a vacuum is called free expansion; essentially it is expansion which is not restrained by an opposing force.

- Let us consider a gas separated from the vacuum by a partition. Let the partition be removed. The gas rushes to fill the entire volume.



Unrestrained Expansion

- Though this free expansion process involves a change of volume yet the work transfer is zero since the vacuum does not offer any resistance to the expansion process.

- Free expansion process is a totally irreversible process for which work transfer is zero even though $\int$ pdv is not zero.

Heat Transfer:

- Heat is defined as the form of energy that is transferred across a boundary by virtue of temperature difference. The temperature difference is the ‘potential’ or ‘force’ and heat transfer is the ‘flux’.

- Heat flow into a system is taken to be positive, and heat flow out of a system is taken as negative. The symbol Q is used for heat transfer.

- Like work transfer, heat transfer is a path function and is an inexact differential.

- A process in which no heat crosses the boundary of the system is called an adiabatic process.

- Thus, an adiabatic process is one in which there is only work interaction between the system and its surroundings.

- A wall which is impermeable to the flow of heat is an adiabatic wall, whereas a wall which permits the flow of heat is a diathermic wall.

Specific Heat:

- The specific heat of a substance is defined as the amount of heat required to raise a unit mass of the substance through a unit rise in temperature. The symbol c will be used for specific heat.

$$C = \frac{Q}{m\Delta T} \qquad \text{J/kg K.}$$

- For gases, if the process is at constant pressure, it is c_p, and if the process is at constant volume, it is c_v.

- For solids and liquids, however, $c_p=c_v=c$, as they are incompressible.

Latent Heat:

- The latent heat is the amount of heat transfer required to cause a phase change in unit mass of a substance at a constant pressure and temperature.

- There are three phases in which matter can exist; solid, liquid, and vapour or gas.

- The latent heat of fusion (L_{fu}) is the amount of heat transferred to melt unit mass of solid into liquid, or to freeze unit mass of liquid to solid.

- The latent heat of vaporization (L_{vap}) is the quantity of heat required to vaporise unit mass of liquid into vapour or condense unit mass of vapour into liquid.

- The latent heat of sublimation (L_{sub}) is the amount of heat transferred to convert unit mass of solid to vapour or vice versa.

- L_{fu} is not much affected by pressure, whereas L_{vap} is highly sensitive to pressure.

Comparison of Heat and Work:

Similarities:

- Both heat and work are path function; they are not properties of the system and their differentials are not exact.

- They represent energy crossing the system boundary; and hence they are a boundary phenomenon.

- Both represent transient phenomenon; these energy interactions occur only when a system undergoes change of state. They exist as stored energy before or after the interaction.

- Concepts of heat and work are associated not with a ‘store’ but with a ‘transfer across boundary’.

Dissimilarities:

- There cannot be work transfer in a stable system. No such restriction exists for heat interaction.

- Heat is energy interaction due to temperature difference only; work is by reasons other than temperature difference.

- Heat is a low grade energy whereas work is a high grade energy.

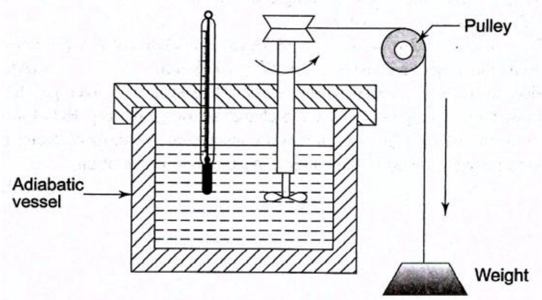
EENGINEERING THERMODYNAMICS

Unit – II

Learning Material

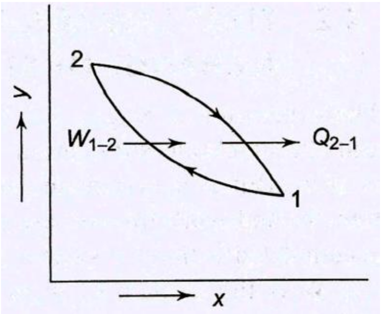
The first Law of Thermodynamics for a Control Mass Undergoing a Cycle - Joule's Experiment

- Consider a closed system consisting of known mass of water, m, contained in an adiabatic vessel having a thermometer and a paddle wheel, as shown in fig.2.3.



Adiabatic Work

- Let a certain amount of work W_{1-2} be done upon the system by the paddle wheel. The quantity of work can be measured by the fall of weight which drives the paddle wheel through a pulley.
- Let the system is initially at temperature T_1, the same as that of atmosphere, and after work transfer let the temperature rise to T_2. The pressure is always 1 atm.
- The process 1-2 undergone by the system is shown in fig. in generalized thermodynamic coordinates, X, Y.



Adiabatic Work Transfer W_{1-2} Followed by Heat Transfer Q_{2-1}

- Let the insulation now be removed. The system and the surroundings interact by heat transfer till the system returns to the original temperature T_1, attaining the condition of thermal equilibrium with the atmosphere.
- The amount of heat transfer Q_{2-1} from the system during this process, 2-1, shown in fig. can be estimated from $Q_{2-1} = m\, c_p\, (T_2 - T_1)$.
- The system thus executes a cycle, which consists of definite amount of work input W_{1-2} to the system followed by the transfer of an amount of heat Q_{2-1} from the system.

- It has been found that this W_{1-2} is always proportional to the heat Q_{2-1}, and the constant of proportionality is called the Joule's equivalent or the mechanical equivalent of heat.
- In the simple example given here, there are only to energy transfer quantities as the system performs a thermodynamic cycle. If the cycle involves many more heat and work quantities, the same result will be found. Expressed algebraically.

$$\left(\sum W\right)_{cycle} = \left(\sum Q\right)_{cycle}$$

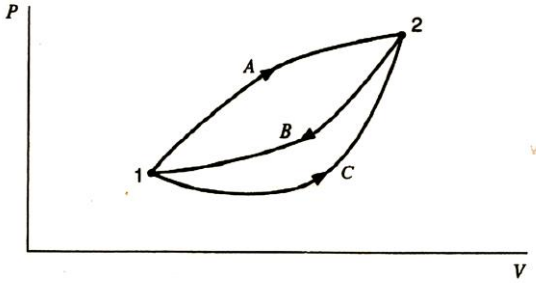
- This is also expressed in the form

$$\oint dW = J \oint dQ$$

- Where the symbol $\oint$ denotes the cyclic integral for the closed path. This is the first law for a closed system undergoing a cycle. It is accepted as a general law of nature. Since no violation of it has ever been demonstrated.
- *The first law of thermodynamics states that during any cycle a system (Control mass) undergoes, the cyclic integral of the heat is equal to the cyclic integral of the work.*

The First Law of Thermodynamics for a Change in State of a Control Mass

- Consider a system that undergoes a cycle in which it changes from state 1 to state 2 by process A and returns from state 2 to state 1 by process B. This cycle is shown in Fig. on a pressure – volume diagram.



Demonstration of the Existence of Thermodynamic Property E

- From the first law of thermodynamics

$$\oint \delta Q = \oint \delta W$$

- Considering the two separate processes, we have $\int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B$
- Now consider another cycle in which the control mass changes from state 1 to state 2 by process C and returns to state 1 by process B, as before. For this cycle we can write $\int_1^2 \delta Q_C + \int_2^1 \delta Q_B = \int_1^2 \delta W_C + \int_2^1 \delta W_B$

  Subtracting the second of these equations from the first, we obtain $\int_1^2 \delta Q_A - \int_1^2 \delta Q_C = \int_1^2 \delta W_A - \int_1^2 \delta W_C$

  or by rearranging, $\int_1^2 (\delta Q - \delta W)_A = \int_1^2 (\delta Q - \delta W)_C$

- Since A and C represent arbitrary processes between states 1 and 2, the quantity $(\delta Q - \delta W)$ is the same for all processes between states 1 and 2. Therefore, $(\delta Q - \delta W)$ depends only on the initial and final states and not on the path followed between the two states. We conclude that this is a point function, and therefore it is the differential of a property of the mass. This property is the energy of the mass and is given the symbol E. Thus we can write dE = $\delta Q - \delta W$
- Because E is property, its derivative is written dE. When equation is integrated from an initial state 1 to a final state 2, we have $E_2 - E_1 = Q_{1-2} - W_{1-2}$
- Where E_1 and E_2 are the initial and final values of the energy E of the control mass, Q_{1-2} is the heat transferred to the control mass during the process from state 1 to state 2, and W_{1-2} is the work done by the control mass during the process.
- The physical significance of the property E is that it represents all the energy of the system in the given state. This energy might be present in a variety of forms, such as the kinetic or potential energy of the system as a whole with respect to the chosen coordinate frame, energy associated with the motion and position of the molecules, energy associated with the structure of the atom, chemical energy present in a storage battery, energy present in a charged condenser, or any of a number of other forms.
- E = Internal energy + kinetic energy + potential energy (or)
- E = U + KE + PE
- $dE = dU + d(KE) + d(PE) = \delta Q - \delta W$
- In words this equation states that as a control mass undergoes a change of state, energy may cross the boundary as either heat or work, and each may be positive or negative. The net change in the energy of the system will be exactly equal to the net energy that crosses the boundary of the system. The energy of the system may change in any or three ways – by a change in internal energy, in kinetic energy, or in potential energy.
- The kinetic energy is expressed as $KE = \frac{1}{2}mV^2$, where V is the velocity of the system as a whole.
- The potential energy is expressed as $PE = mgZ$, where Z is the altitude of the center of gravity of the system as a whole from the datum line.

- Therefore, the fist law thermodynamics for a change of state of the system is expressed as

$$U_2 - U_1 + \frac{m(V_2^2 - V_1^1)}{2} + mg(Z_2 - Z_1) = Q_{1-2} - W_{1-2}$$

- *The net change of the energy of the control mass during a process is always equal to the net transfer of energy across the boundary as heat and work.*

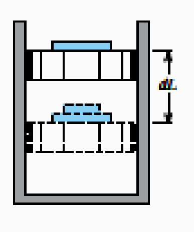
Internal Energy – A thermodynamic Property

- Internal energy is an extensive property because it depends on the mass of the system. Similarly, kinetic and potential energies are extensive properties.

- The symbol *U* designates the internal energy of a given mass of substance.
- The internal energy per unit mass, u, is the intensive property of the system.

The Thermodynamic Property Enthalpy

- Let us consider a control mass undergoing a quasi-equilibrium constant-pressure process, as shown in fig.



Constant-Pressure Quasi-equilibrium Process

- Assume that there are no changes in kinetic or potential energy and that the only work done during the process is that associated with the boundary (piston) movement. Taking the gas as control mass and applying the first law as

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

- The work done can be calculated from the relation $W_{1-2} = \int_1^2 PdV$
- Since the pressure is constant, $W_{1-2} = P\int_1^2 dV = P(V_2 - V_1)$
- Therefore, $Q_{1-2} = U_2 - U_1 + P_2V_2 - P_1V_1$

  $= (U_2 + P_2V_2) - (U_1 + P_1V_1)$

- We find that, in this very restricted case, the heat transfer during the process is given in terms of the change in the quantity (U + PV) between the initial and final states.
- Because all these quantities are thermodynamic properties, that is, functions only of the state of the system, their combination must also have these same characteristics. Therefore, we find it convenient to define a new extensive property, the enthalpy, H = U + PV or, per unit mass, h = u + pv
- The heat transfer in a constant-pressure quasi-equilibrium process is equal to the change in enthalpy, which includes both the change in internal energy and the work for this particular process.

The First Law as a Rate Equation

- $\frac{dU}{dt} + \frac{d(KE)}{dt} + \frac{d(PE)}{dt} = \dot{Q} - \dot{W}$
- In the absence of kinetic and potential energies, $\frac{dE}{dt} = \dot{Q} - \dot{W}$

Energy of an isolated system

- An isolated system is one in which there is no interaction of the system with the surroundings.
- For an isolated system dQ = 0, dW=0. Hence, application first law of thermodynamics gives dE = 0. Therefore, E = constant.

- The energy of an isolated system is always constant.

Perpetual Motion Machine of the First Kind – PMM1

- There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously. Such a fictitious machine is called a perpetual motion machine of the first kind, or in brief, PMM1. A PMM1 is thus impossible.

The Constant-Volume and Constant-Pressure Specific Heats

- The specific heat at constant volume is defined as the amount of heat required to raise the temperature of 1 kg substance by 1 degree when volume is maintained constant $C_v = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_v$.
- Constant volume, for which the work term (P dV) is zero, so that the specific heat at constant volume can also be expressed as $C_v = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$
- The specific heat at constant pressure is defined as the amount of heat required to raise the temperature of 1 kg substance by 1 degree when pressure is maintained constant $C_p = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_p$
- Constant pressure, for which the work term can be integrated and the resulting PV terms at the initial and final states can be associated with the internal energy terms, thereby leading to the conclusion that the heat transfer can be expressed in terms of the enthalpy change. The corresponding specific heat at constant pressure can be expressed as $C_p = \frac{1}{m}\left(\frac{\delta Q}{\delta T}\right)_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p$

Relationship between Specific Heats and Gas Constant

- The enthalpy, h = u + pv.

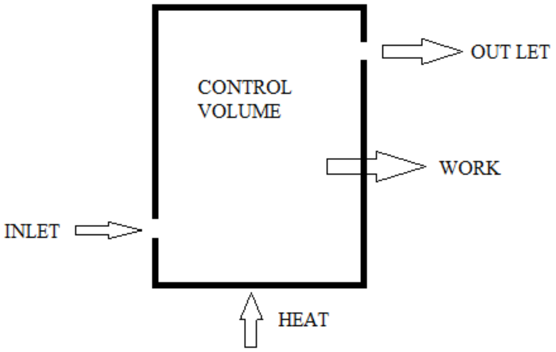
  = u + RT
- dh = du + RdT

  Therefore, $\frac{dh}{dT} = \frac{du}{dT} + R$

  $$c_p = c_v + R; \quad c_p - c_v = R$$

First-Law Analysis for a Control Volume

- For an open system, mass as well as heat and work can cross the control surface, and the mass in the control volume can change with time.



Flow Process and Control Volume

- Applying the law of conservation of mass to the control volume with several possible flows as

$$\frac{dm_{C.V.}}{dt} = \sum \dot{m}_i - \sum \dot{m}_e$$

- The extension of the first law of thermodynamics becomes

$$\frac{dE_{C.V.}}{dt} = \dot{Q}_{C.V.} - \dot{W}_{C.V.} + \dot{m}_i(e_i + p_i v_i) - \dot{m}_e(e_e + p_e v_e)$$

$$= \dot{Q}_{C.V.} - \dot{W}_{C.V.} + \dot{m}_i\left(h_i + \frac{1}{2}V_i^2 + gZ_i\right) - \dot{m}_e\left(h_e + \frac{1}{2}V_e^2 + gZ_e\right)$$

- For a control volume with several entering and leaving mass flow rates,

$$\frac{dE_{C.V.}}{dt} = \dot{Q}_{C.V.} - \dot{W}_{C.V.} + \sum \dot{m}_i\left(h_i + \frac{1}{2}V_i^2 + gZ_i\right) - \sum \dot{m}_e\left(h_e + \frac{1}{2}V_e^2 + gZ_e\right)$$

The steady-State Process

- The control volume does not move relative to the coordinate frame.
- The state of the mass at each point in the control volume does not vary with time.
- As for the mass that flows across the control surface, the mass flux and the state of this mass at each discrete area of flow on the control surface do not vary with time.
- The rates at which heat and work cross the control surface remain constant.
- Therefore, $\frac{dm_{C.V.}}{dt} = 0$ and also $\frac{dE_{C.V.}}{dt} = 0$
- The first-law for a control volume under steady-state with several entering and leaving mass flow rates is expressed as

$$\dot{Q}_{C.V.} + \sum \dot{m}_i\left(h_i + \frac{V_i^2}{2} + gZ_i\right) = \sum \dot{m}_e\left(h_e + \frac{V_e^2}{2} + gZ_e\right) + \dot{W}_{C.V.}$$

- Many of the engineering applications of the steady-state model involve only on flow stream entering and leaving the control volume. For this type of process, we can write

$$\dot{Q}_{C.V.} + \dot{m}\left(h_i + \frac{V_i^2}{2} + gZ_i\right) = \dot{m}\left(h_e + \frac{V_e^2}{2} + gZ_e\right) + \dot{W}_{C.V.}$$

  Rearranging this equation, we have

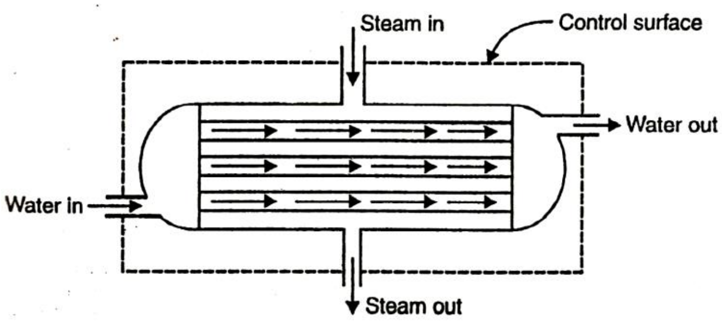
$$q + h_i + \frac{V_i^2}{2} + gZ_i = h_e + \frac{V_e^2}{2} + gZ_e + w$$

  Where, *q* and *w* are heat and work interactions per unit mass flow rate.

Examples of Steady-State Processes

a) Heat Exchanger

- A heat exchanger is device in which heat transferred from one fluid to another. One such example is the steam condenser, where steam condenses outside the tubes and cooling water flows through the tubes, as shown in figure 2.5.



Schematic Diagram of a Steam Condenser

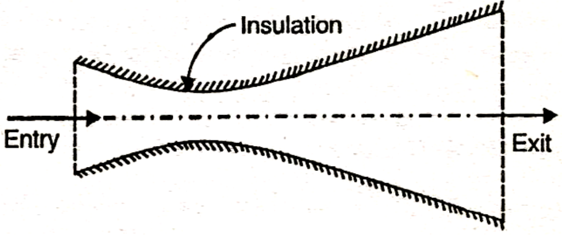
- The flow through a heat exchanger is characterized by
  - (a) the Heat exchange process tends to occur at constant pressure and frictional pressure drop in the tubes is neglected.
  - (b) there is no means for doing any work (shaft work, electrical work, etc.) and
  - (c) changes in kinetic and potential energies are negligibly small.
  - (d) no external heat interaction.
- Using the subscripts 's' for steam and 'w' for water and applying the steady flow energy equation for the heat exchanger, we get

$$\dot{m}_s(h_i)_s + \dot{m}_w(h_i)_w = \dot{m}_s(h_e)_s + \dot{m}_w(h_e)_w \qquad \text{or}$$

$$\dot{m}_s(h_i - h_e)_s = \dot{m}_w(h_e - h_i)_w$$

b) Nozzle and diffuser

- A nozzle is a steady-state device whose purpose is to create high velocity fluid stream at the expense of the fluid pressure.
- A diffuser is a steady-state device whose purpose is to raise the pressure of the fluid at the expense of fluid velocity.



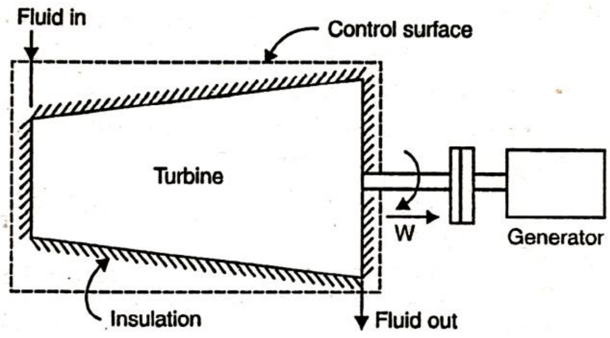
Schematic Diagram of a Nozzle

- The flow through a nozzle is characterized by the following features:
  - (a) There is no means to do any work
  - (b) There is little or no change in potential energy.
  - (c) There is usually little or no heat transfer. An exception is the large nozzle on a liquid-propellant rocket.
- With these assumptions, the steady flow energy equation for the case of nozzle or diffuser becomes

$$h_i + \frac{V_i^2}{2} = h_e + \frac{V_e^2}{2}$$

c) Steam or Gas Turbine

- A turbine is a rotary steady-state machine whose purpose is to produce shaft work at the expense of the pressure of the working fluid. Two general classes of turbines are steam turbines and gas turbines.



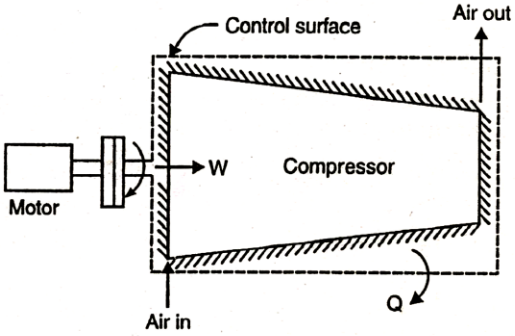
Schematic Diagram of a Turbine

- The characteristic features of flow through a steam or gas turbine are:
  a) There is little or no change in potential energy.
  b) There is usually little or no heat transfer.
  c) There is little or no change in kinetic energy.
- With these assumptions, the steady flow energy equation for the case of turbine becomes

$$\dot{m}h_i = \dot{m}h_e + \dot{W}_{shaft}$$

d) Rotary Compressor

- The purpose of the steady state compressor is to increase the pressure of a fluid by putting in shaft work. The most common is a rotary type compressor (either axial flow or radial / centrifugal flow).



Schematic Diagram of a Rotary Compressor

- The characteristic features of flow through a rotary compressor are
  a) Shaft work is done on the system and the fluid is compressed; *W* is negative.
  b) Heat is lost to the surroundings; *Q* is negative
  c) There is little or no change in potential energy.
- With these assumptions, the steady flow energy equation may be written as

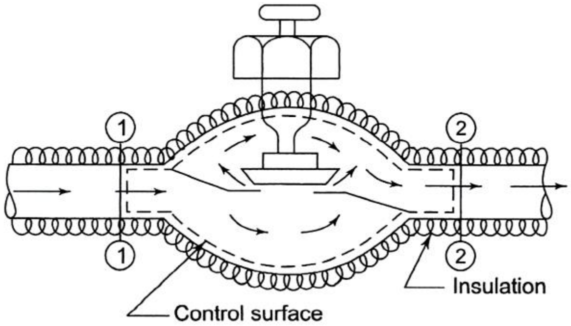
$$\dot{m}(h_i + \frac{V_i^2}{2}) - \dot{Q} = \dot{m}(h_e + \frac{V_e^2}{2}) - \dot{W}_{shaft}$$

If the velocity changes are neglected and the flow process is treated as adiabatic (Q=0), then

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

e) Throttling Device

- When a fluid flows through a restricted passage, like a partially opened wall, an orifice, or a porous plug, there is an appreciable drop in pressure, and the flow is said to be throttled. Figure 2.8 shows the process of throttling by a partially opened valve on a fluid following in an insulated pipe.



Flow through a Valve

- The flow through a throttling device is characterized by the following features:
  - a) There is no means to do any work.
  - b) There is little or no change in potential energy.
  - c) There is usually little or no heat transfer.
- With these assumptions, the steady flow energy equation may be written as

$$(h_i + \frac{V_i^2}{2}) = (h_e + \frac{V_e^2}{2})$$

- Often the velocities in throttling are so low that the kinetic energy terms are also negligible. So

$$h_i = h_e$$

- Therefore, throttling process is an isenthalpic process for which enthalpy remains constant.

Engineering Thermodynamics

Unit – III

Learning Material

Limitations of First Law of Thermodynamics

- First law fixes the exchange rate between heat and work, and places no restrictions on the direction of change.
- Processes proceed spontaneously in certain directions, but the reverse is not automatically attainable even though the reversal of the processes does not violate the first law.
- First law provides a necessary but not a sufficient condition for a process to occur, and
- There does exist some directional law which would tell whether a particular process occurs or not. Answer is provided by the second law of thermodynamics.

Thermal Reservoir

- A thermal (heat) reservoir is that part of environment which can exchange heat energy with a system. It has sufficiently large heat capacity and its temperature is not affected by the quantity of heat transferred to or from it.
- A thermal reservoir is thus characterized by its temperature which remains constant.
- The reservoir which is at high temperature and supplies heat is known as heat source. Examples are a boiler furnace, a combustion chamber and a nuclear reactor, etc.
- The reservoir which is at low temperature and to which heat is transferred is called the heat sink. Atmospheric air, ocean and river etc. constitute the heat sink.

Heat Engine

- A heat engine may be defined as a device that operates in a thermodynamic cycle and does a certain amount of net positive work through the transfer of heat from a high-temperature body to a low-temperature body
- The internal combustion engine and the gas turbine are examples of such devices.
- Another example of a heat engine is the thermoelectric power generation device.

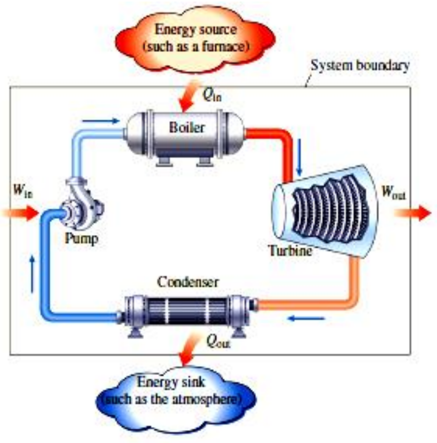


Fig. 3.1: A Simple Steam Power Cycle

- Thermal efficiency is defined as the ratio of net work output to heat input

$$\eta_{thermal} = \frac{Network\ output}{Heat\ input} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H}$$

- Typical values for the thermal efficiency of real engines are about 35-50% for large power plant, 30-35% for gasoline engines, and 35-40% for diesel engines.

Refrigerator or Heat Pump

- A refrigerator or heat pump may be define as a device that operates in a thermodynamic cycle and transfer heat from a low-temperature space or body to a high-temperature space or body by receiving work energy as input.
- The purpose of the refrigerator is to maintain the space at a temperature lower than the surroundings by extracting heat from it.

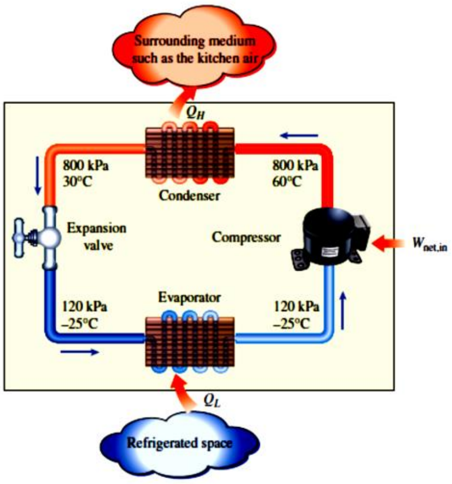


Fig. 3.2: A Simple Refrigeration Cycle

- The purpose of the heat pump is to maintain the space at a temperature higher than the surroundings by supplying heat to it.
- The “efficiency” of a refrigerator or heat pump is expressed in terms of the coefficient of performance, which we designate as COP.
- The coefficient of performance is defined as the ratio of desired effect to the work input.
- For a refrigerator, the desired effect is the amount of heat extracted from a low temperature space, Q_L. Thus, the COP of a refrigerator is

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

- For a heat pump, the desired effect is the amount of heat supplied to a high temperature space, Q_H. Thus, the COP of a heat pump is

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

- The relationship between COP of heat pump and COP of refrigerator is derived as

$$(COP)_{HP} = \frac{Q_H}{W} = \frac{Q_L + W}{W} = 1 + \frac{Q_L}{W} = 1 + (COP)_R$$

The Second Law of Thermodynamics

- **The Kelvin-Planck statement**: It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.

- This statement ties in with our discussion of the heat engine. It states that it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high-temperature body, and does an equal amount of work. The only alternative is that some heat must be transferred from the working fluid to a low-temperature body.
- This implies that it is impossible to build a heat engine that has thermal efficiency of 100%
- **The 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 cooler body to a hotter body.
- This statement is related to the refrigerator or heat pump. It states that it is impossible to construct a refrigerator that operates without input of work. This also implies that the coefficient of performance is always less than infinity.

Perpetual-Motion Machine of Second Kind

- A perpetual-motion machine of the second kind would extract heat from a source and then convert this heat completely into other forms of energy, thus violating the second law.

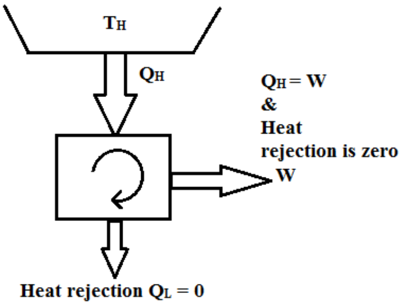


Fig. 3.3: Perpetual-Motion Machine of Second Kind

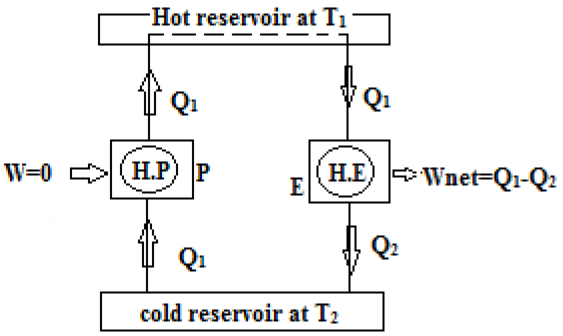
- Perpetual-motion machine of second kind has 100% thermal efficiency.

Equivalence of Kelvin Planck and Classius statement

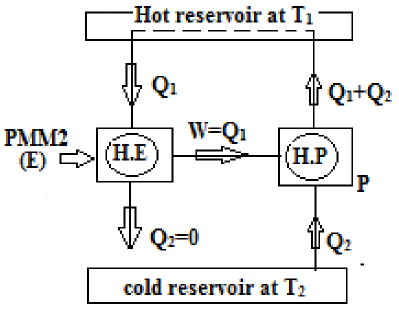
At first Kelvin-Planck's and classius statements may appear to be unconnected, but it can easily be shown that they are virtually two parallel statements of the second law and are equivalent in all respects.

The equivalence of the two statements will be proved if it can be shown that the violation of one statement implies the violation of the second, and vice versa.

1. Let us first consider a cyclic heat pump P which transfers heat from a low temperature reservoir (T_2) to a high temperature reservoir (T_1) with no other effect, i.e., with no expenditure of work, ***violating classius statement***. Let us assume a cyclic heat engine E operating between the same thermal reservoirs, producing W_{net} in one cycle. The rate of working of the engine is such that it draws an amount of heat Q_1 from the hot reservoir equal to that discharged by the heat pump. Then the hot reservoir may be eliminated and the heat Q_1 discharged by the heat pump is fed to the heat engine. So we see that the heat pump P and the heat engine E acting together constitute a heat engine operating in cycles and producing net work while exchanging heat only with one body at a single fixed temperature (T_2). This violates Kelvin-Planck Statement.



Violation of the classius statement



Violation of Kelvin-Planck statement

2. Let us now consider a perpetual motion machine of second kind (E) which produces net work in a cycle by exchanging heat with only one thermal reservoir (at T_1) and thus violates the Kelvin-planck statement. Let us assume a cyclic heat pump (P) extracting heat Q_2 from a low temperature reservoir at T_2 and discharging heat to a high temperature reservoir at T_1 with the expenditure of work W equal to what the PMM2 delivers in a complete cycle. So E and P together constitute a heat pump working in cycles and producing the sole effect of transferring heat from a lower to a higher temperature body, thus violating the classius statement.

Carnot Cycle and Carnot Heat Engine

A Carnot cycle is a hypothetical cycle consisting of four distinct processes: two reversible isothermal processes and two reversible adiabatic processes. The cycle was proposed in 1824 by a young French engineer, Sadi Carnot.

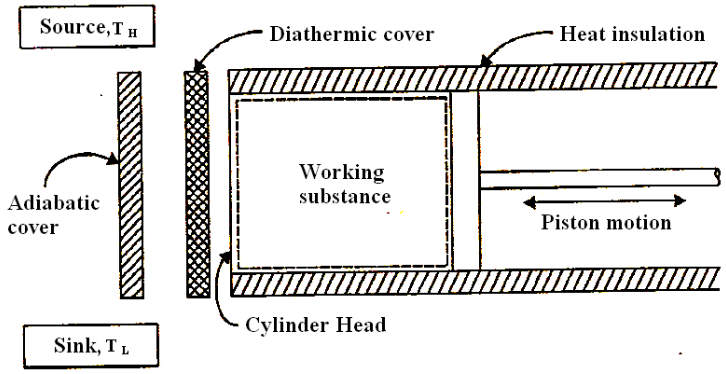


Fig. 3.4a: Essential Elements of a Heat Engine working on Carnot Cycle

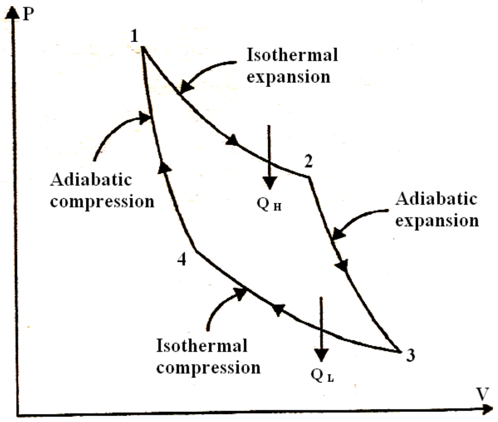


Fig. 3.4b: Carnot Heat Engine Cycle on P-V plot

The sequence of operation for the different processes constituting a Carnot Cycle is:

Isothermal expansion (1 – 2): The heat is supplied to the working fluid at constant temperature T_H. This is achieved by bringing the heat source in good thermal contact with the cylinder head through diathermic cover. The gas expands isothermally from state point 1 to state point 2.

The heat supplied equals the work done which is represented by area under the curve 1-2 on pressure-volume plot and is given by

$$Q_H = W_{1-2} = p_a V_1 log_e \frac{V_2}{V_1} = m\,R\,T_1 log_e \frac{V_2}{V_1}$$

Adiabatic Expansion (2-3): At the end of isothermal expansion (state point 2), the heat source is replaced by adiabatic cover. The expansion continues adiabatically and reversibly up to state point 3. Work is done by the working fluid at the expense of internal energy and its temperature falls to T_L at state point 3.

Isothermal Compression (3-4): After state point 3, the piston starts moving inwards and the working fluid is compressed isothermally at temperature T_L. The constant temperature T_L is maintained by removing the adiabatic cover and bringing the heat sink in contact with the cylinder head. The compression continues up to state point 4.

The working fluid loses heat to the sink and its amount equals the work done on the working fluid. This work is represented by area under the curve 3 - 4 and its amount is given by.

$$Q_L = W_{3-4} = p_3 V_3 log_e \frac{V_3}{V_4} = m\,R\,T_3 log_e \frac{V_3}{V_4}$$

Adiabatic Compression (4 – 1): At the end of isothermal compression (state point 4), the heat sink is removed and is replaced by adiabatic cover. The compression now proceeds adiabatically and reversibly till the working fluid returns back to its initial state point 1. Work is done on the working fluid, the internal energy increases and temperature is raised to T_H.

Since all the processes that constitute a Carnot cycle are reversible, the Carnot cycle is referred to as a reversible cycle. The thermal efficiency of Carnot heat engine is given by

$$\eta = \frac{net\ work\ output}{heat\ input} = \frac{W_{net}}{Q_H}$$

There are no heat interactions along the reversible adiabatic processes 2 – 3 and 4 – 1, and application of the first law of thermodynamics for the complete cycle gives.

$$\oint \delta W = \oint \delta Q \qquad \text{or}$$

$$W_{net} = Q_H - Q_L = mRT_1 log_e \frac{V_2}{V_1} - mRT_3 log_e \frac{V_3}{V_4}$$

Therefore, $$\eta = \frac{mRT_1 log_e \frac{V_2}{V_1} - mRT_3 log_e \frac{V_3}{V_4}}{mRT_1 log_e \frac{V_2}{V_1}} = 1 - \frac{T_3}{T_1} X \frac{log_e \frac{V_3}{V_4}}{log_e \frac{V_2}{V_1}}$$

For the adiabatic expansion processes 2 – 3 and 4 – 1,

$$\frac{T_2}{T_3} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} and\ \frac{T_1}{T_4} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

Since $T_1 = T_2 = T_H$ and $T_3 = T_4 = T_L$, we have $\frac{V_3}{V_2} = \frac{V_4}{V_1}\ or\ \frac{V_3}{V_4} = \frac{V_2}{V_1}$

Substituting the above relation 3.10 in the equation 3.9, we get

$$\eta = 1 - \frac{T_3}{T_1} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H}$$

Following conclusions can be made with respect to efficiency of a Carnot engine:

(1) The efficiency is independent of the working fluid and depends upon the temperatures of source and sink.

(2) The efficiency is directly proportional to temperature difference (T_1 – T_2) between the source and the sink.

(3) Higher the temperature difference between source and sink, the higher will be the efficiency.

(4) The efficiency increases with an increase in temperature of source and a decrease in temperature of sink.

(5) If $T_1 = T_2$, no work will be done and efficiency will be zero.

Metallurgical considerations and the high cost of temperature resisting materials limit the higher temperature T_1. The lower temperature T_2 is limited by atmospheric or sink conditions.

Reversed Heat Engine (Carnot Heat Pump or Refrigerator)

Refrigerators and heat pumps are reversed heat engines.

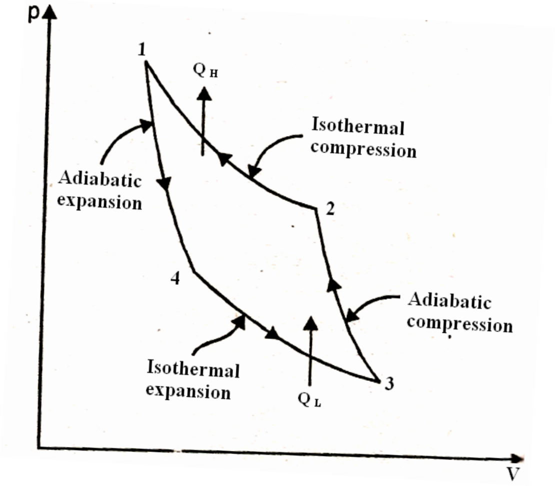


Fig. 3.5: Carnot Heat Pump or Refrigerator Cycle on P-V plot

Fig. 3.5 shows the P – V plot of a Carnot heat pump (i.e. reversed Carnot heat engine). The sequence of operation is:

1 – 4: Isentropic (reversible adiabatic) expansion of working fluid in the clearance space of the cylinder. The temperature falls from T_1 and T_2.

4 – 3: Isothermal expansion during which heat Q_L is absorbed at temperature T_2 from the space being cooled.

3 – 2: Isentropic compression of working fluid. The temperature rises from T_2 to T_1.

3 – 1: Isothermal compression of working fluid during which heat Q_H is rejected to a system at higher temperature.

As outlined above i.e. in the case of heat engine,

$$Q_H = mRT_1 log_e \frac{V_2}{V_1};\ \ Q_L = mRT_3 log_e \frac{V_3}{V_4}$$

Also $\frac{V_3}{V_4} = \frac{V_2}{V_1}$, $T_1 = T_2 = T_H$ and $T_3 = T_4 = T_L$

Therefore, for a heat pump

$$(\text{COP})_{\text{Heat pump}} = \frac{Q_H}{Q_H - Q_L}$$

$$= \frac{mRT_1 log_e \frac{V_2}{V_1}}{mRT_1 log_e \frac{V_2}{V_1} - mRT_3 log_e \frac{V_3}{V_4}} = \frac{T_1}{T_1 - T_3} = \frac{T_H}{T_H - T_L}$$

For a refrigerator,

$$(\text{COP})_{\text{Refrigerator}} = \frac{Q_L}{Q_H - Q_L}$$

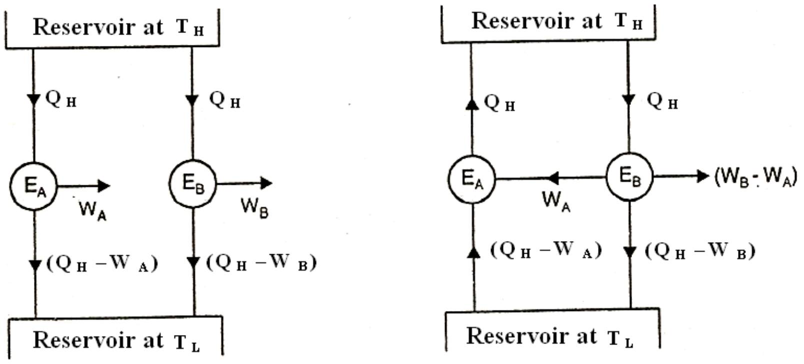
$$= \frac{mRT_3 log_e \frac{V_3}{V_4}}{mRT_1 log_e \frac{V_2}{V_1} - mRT_3 log_e \frac{V_3}{V_4}} = \frac{T_3}{T_1 - T_3} = \frac{T_L}{T_H - T_L}$$

Carnot Theorem

No heat engine operating in a cycle between two given thermal reservoirs, with fixed temperatures, can be more efficient than a reversible engine (Carnot Engine) operating between the same thermal reservoirs.

Proof of Carnot Theorem

Consider a reversible engine E_A and an irreversible engine E_B operating between the same thermal reservoirs at temperatures T_H and T_L. For the same quantity of heat Q_H withdrawn from the high temperature source, the work output from these engines is W_A and W_B respectively. As such the heat given off by the reversible engine is $(Q_H - W_A)$ and that from irreversible engine is $(Q_H - W_B)$.



(a) (b)

Fig. 3.6: Proof of Carnot Theorem

Let it be presumed that the irreversible engine E_B is more efficient than the reversible engine E_A. Then $\frac{W_B}{Q_H} > \frac{W_A}{Q_H}; W_B > W_A \; and \; (Q_H - W_A) > (Q_H - W_B) i.e.,$ work output from irreversible engine is more than that from reversible engine.

Let the reversible engine E_A now be made to operate as a refrigerator or heat pump; the irreversible engine continues to operate as an engine.

Since engine E_A is reversible, the magnitudes of heat and work interactions will remain the same but their direction will be reversed. The work required to drive the refrigerator can be withdrawn from the irreversible engine by having a direct coupling between the two. Fig (b) shows the work and heat interactions for the composite system constituted by the reversible engine (now operating as refrigerator) and the irreversible engine. The net effect is

- No net interaction with the high temperature heat reservoir. It supplies and recovers back the same amount of heat.
- The composite system withdraws $(Q_H - W_A) - (Q_H - W_B) = (W_B - W_A)$ units of heat from the low temperature reservoir and converts that into equivalent amount of work output.

The combination thus constitutes a perpetual motion of the second kind in violation of the second law. Obviously the assumption that the irreversible engine is more efficient than the reversible engine is wrong. Hence, an irreversible engine cannot have efficiency higher than that from a reversible engine operating between the same thermal reservoirs.

Corollaries of Carnot's Theorem:

Corollary 1: All reversible engines operating between the two given thermal reservoirs, with fixed temperature, have the same efficiency.

Corollary 2: The efficiency of any reversible heat engine operating between two reservoirs is independent of the nature of working fluid and depends only on the temperature of the reservoirs.

The Thermodynamic Temperature Scale

- The concept of thermodynamic temperature scale may be developed with the help of figure 3.7, which shows three reservoirs and three engines that operate on the Carnot cycle.

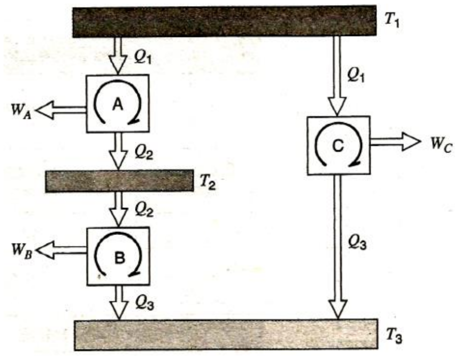


Fig. 3.7: Arrangement of heat engines to demonstrate the Thermodynamic Temperature scale

- T_1 is the highest temperature, T_3 is the lowest temperature, and T_2 is an intermediate temperature, and the engines operate between the various reservoirs as indicated. Q_1 is the same for both A and C and, since we are dealing with reversible cycles, Q_3 is the same for B and C. Since the efficiency of a Carnot cycle is a function only of the temperature, we can write

$$\eta_{thermal} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} = 1 - \psi(T_L, T_H)$$

Where ψ designates a functional relation. Let us apply this functional relation to the three Carnot Cycles shown in figure 3.7.

$$\frac{Q_1}{Q_2} = 1 - \psi(T_{1,}T_2); \qquad \frac{Q_2}{Q_3} = 1 - \psi(T_{2,}T_3); \qquad \frac{Q_1}{Q_3} = 1 - \psi(T_{1,}T_3)$$

Since $\frac{Q_1}{Q_3} = \frac{Q_1 Q_2}{Q_2 Q_3}$

It follows that $\psi(T_1, T_3) = \psi(T_1, T_2) \times \psi(T_2, T_3)$

Note that the left side is a function of T_1 and T_3 (and not of T_2), and therefore the right side of this equation must also be a function of T_1 and T_3 (and not of T_2). From this fact we can conclude that the form of the function ψ must be such that

$$\psi(T_1, T_2) = \frac{f(T_1)}{f(T_2)}; \qquad \psi(T_2, T_3) = \frac{f(T_2)}{f(T_3)}$$

For in this way $f(T_2)$ will cancel from the product of $\psi(T_{1,}T_2) \times \psi(T_2, T_3)$. Therefore, we conclude that $\frac{Q_1}{Q_3} = \psi(T_1, T_3) = \frac{f(T_1)}{f(T_3)}$

In general terms, $\frac{Q_H}{Q_L} = \frac{f(T_H)}{f(T_L)}$

Suppose we had a heat engine operating on the Carnot cycle that received heat at the temperature of the steam point and rejected heat at the temperature of the ice point. The efficiency of such an engine could be measured to be 26.8%,

$$\eta_{th} = 1 - \frac{T_L}{T_H} = 1 - \frac{T_{ice\ point}}{T_{steam\ point}} = 0.2680$$

$$\frac{T_{ice\ point}}{T_{steam\ point}} = 0.7320$$

This gives us one equation concerning the two unknowns T_H and T_L. The second equation comes from the difference between the steam point and ice point.

$$T_{\text{steam point}} - T_{\text{ice points}} = 100$$

Solving these two equations simultaneously, we find

$$T_{\text{steam point}} = 373.15 \text{ K} \text{ and } T_{\text{ice point}} = 273.15 \text{ K}$$

It follows that, T(°C) + 273.15 = T(K)

The Inequality of Clausius

- The inequality of Clausius is expressed as $\oint \frac{\delta Q}{T} \leq 0$.
- The inequality of Clausius is a corollary or a consequence of the second law of thermodynamics. It will be demonstrated to be valid for all possible cycles, including both reversible and irreversible heat engines and refrigerators.

Consider first a reversible (Carnot) heat engine cycle operating between reservoirs at temperatures T_H and T_L, as shown in Fig. 3.8. For this cycle, the cyclic integral of the heat transfer, $\oint \delta Q$, is greater than zero.

$$\oint \delta Q = Q_H - Q_L > 0$$

Since T_H and T_L are constant, from the definition of the absolute temperature scale and from the fact this is a reversible cycle, it follows that

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

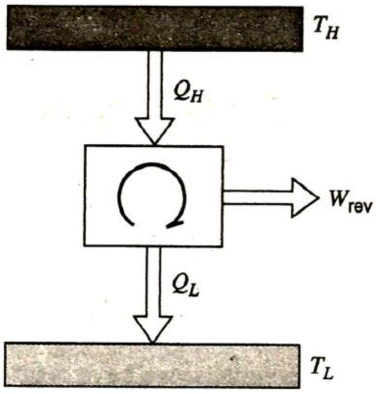


Fig. 3.8: Reversible heat engine cycle for demonstration of the inequality of Clausius

If $\oint \delta Q$, the cyclic integral of δQ, approaches zero (by making T_H approach T_L) and the cycle remains reversible, the cyclic integral of $\delta Q/T$ remains zero. Thus, we conclude that for all reversible heat engine cycles

$$\oint \frac{\delta Q}{T} = 0$$

Now consider an irreversible cyclic het engine operating between the same T_H and T_L as the reversible engine of Fig. 8.1 and receiving the same quantity of heat Q_H. Comparing the irreversible cycle with the reversible one, we conclude from the second law that

$$W_{irr} < W_{rev}$$

Since $Q_H - Q_L = W$ for both the reversible and irreversible cycles, we conclude that

$(Q_H - Q_L)_{irr} < (Q_H - Q_L)_{rev}$ and therefore, $(Q_L)_{irr} > (Q_L)_{rev}$

Consequently, for the irreversible cyclic engine,

$$\oint \delta Q = (Q_H - Q_L)_{irr} > 0$$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{(Q_L)_{irr}}{T_L} < 0$$

Thus, we conclude that for all irreversible heat engine cycles

$$\oint \frac{\delta Q}{T} < 0$$

Therefore, in general, for any heat engine or refrigerator $\oint \frac{\delta Q}{T} \leq 0$

The Significance of the inequality of Clausius may be illustrated by considering the simple steam power plant cycle shown in Fig.3.9.

Heat is transferred in two places, the boiler and the condenser. Therefore,

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T}\right)_{boiler} + \int \left(\frac{\delta Q}{T}\right)_{condenser}$$

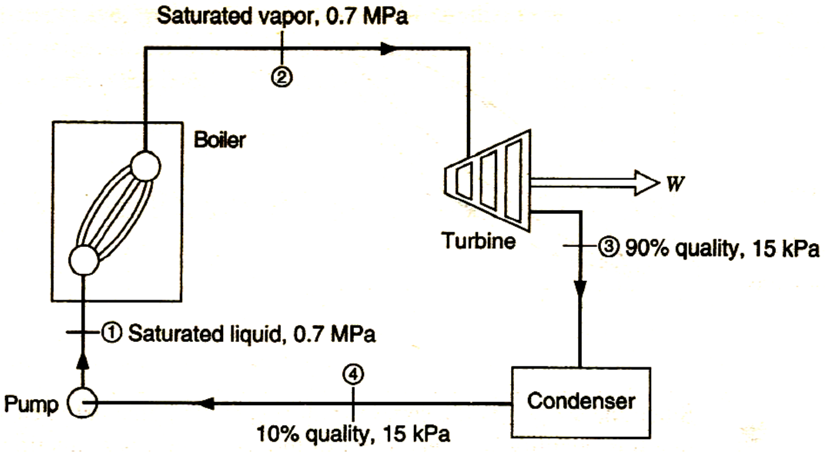


Fig.3.9: A simple Steam Power Plant that demonstrates the Inequality of Clausius

Since the temperature remains constant in both the boiler and condenser, this may be integrated as follows:

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1}\int_1^2 \delta Q + \frac{1}{T_3}\int_3^4 \delta Q = \frac{Q_{12}}{T_1} + \frac{Q_{34}}{T_3}$$

Let us consider a 1 kg mass as the working fluid. We have then

$$q_{12} = h_2 - h_1 = 2066.3\ kJ/kg, \quad T_1 = 164.97^oC$$

$$q_{34} = h_4 - h_3 = 463.4 - 2361.8 = -1898.4\ kJ/kg, \quad T_3 = 53.97^oC$$

Therefore,

$$\oint \frac{\delta Q}{T} = \frac{2066.3}{164.97 + 273.15} - \frac{1898.4}{53.97 + 273.15} = -1.087\ kJ/kg - K$$

Thus, this cycle satisfies the inequality of Clausius, which is equivalent to saying that it does not violate the second law of thermodynamics.

Entropy – A Property of a System

By applying Eq.3.28 and Fig. 3.10 we can demonstrate that the second law of thermodynamics leads to a property of a system that we call entropy.

- *Entropy is a measure of molecular disorderliness of a substance.*

Let a closed system undergo a reversible process from state 1 to state 2 along a path A, and let the cycle be completed along path B, which is also reversible.

Because this is a reversible cycle, we can write

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_B = 0$$

Now consider another reversible cycle, which proceeds first along path C and is then completed along path B. For this cycle we can write

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_C + \int_2^1 \left(\frac{\delta Q}{T}\right)_B = 0$$

Subtracting the equation 3.30 from the equation 3.29, we get

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_A = \int_1^2 \left(\frac{\delta Q}{T}\right)_C$$

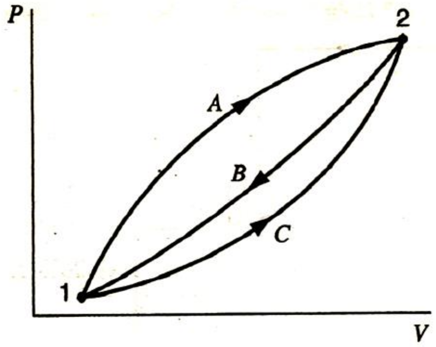


Fig. 3.10: Two reversible cycles demonstrating the fact that entropy is a property of a substance

Since the $\int \delta Q$/T is the same for all reversible paths between states 1 and 2, we conclude that this quantity is independent of the path and it is a function of the end states only; it is therefore a property. This property is called entropy and is designated by 'S'. It follows that entropy may be defined as a property of a substance in accordance with the relation.

$$dS = \left(\frac{\delta Q}{T}\right)_{rev} \qquad \textbf{(Equation 3.32)}$$

- Entropy is an extensive property, and the entropy per unit mass is designated by 's'. The change in the entropy of a system as it undergoes a change of state may be found by integrating Eq.3.32. Thus,

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}$$

- To perform this integration, we must know the relation between T and Q.
- Since entropy is a property, the change in the entropy of a substance in going from one state to another is the same for all processes, both reversible and irreversible, between these two states.
- Equation 3.33 enables us to calculate changes of entropy, but it tells us nothing about absolute values of entropy.
- From the third law of thermodynamics, which is based on observations of low-temperature chemical reactions, it is concluded that the entropy of all pure substances (in the appropriate structural form) can be assigned the absolute value of zero at the absolute zero of temperature.
- It also follows from the subject of statistical thermodynamics that all pure substances in the (hypothetical) ideal-gas state at absolute zero temperature have zero entropy.

Entropy Change of a control mass during a Reversible Process

The entropy change during a reversible process 1 – 2 is given by

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}$$

The relationship between δQ and T can be obtained from the thermodynamics property relations.

The Thermodynamic Property Relations

The two important thermodynamic property relations for a compressible substance can be derived from the first law of thermodynamics.

$$\delta Q = dU + \delta W$$

For a reversible process of simple compressible substance, we can write

$$\delta Q = TdS \text{ and } \delta W = PdV$$

Substituting these relations into the first law equation, we get

$$TdS = dU + PdV$$

Since enthalpy is defined as $= U + PV$, on differentiation we get

$$\mathrm{dH} = \mathrm{dU} + \mathrm{PdV} + \mathrm{VdP}$$

$$= \delta Q + VdP$$

$$= TdS + VdP \qquad \text{or}$$

$$TdS = dH - VdP$$

These equations can also be written for a unit mass,

$$TdS = du + Pdv$$

$$TdS = dh - vdP$$

Entropy Change of a Control Mass during an Irreversible Process

Consider a control mass that undergoes the cycles shown in fig. 3.11.

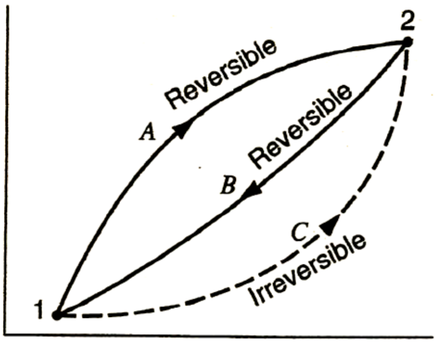


Fig. 3.11: Entropy Change of a Control Mass during an irreversible process

Since the cycle made up of the reversible processes A and B is a reversible cycle, we can write

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_B = 0$$

The cycle made of the irreversible process C and the reversible process B is an irreversible cycle. Therefore, for this cycle the inequality of Clausius may be applied as

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T}\right)_C + \int_2^1 \left(\frac{\delta Q}{T}\right)_{\boldsymbol{B}} < 0$$

Subtracting the equation 3.34 from the equation 3.33 and rearranging, we have

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_A > \int_1^2 \left(\frac{\delta Q}{T}\right)_C$$

Since path A is reversible, and since entropy is a property,

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_A = \int_1^2 dS_A = \int_1^2 dS_C$$

Therefore,

$$\int_1^2 dS_C > \int_1^2 \left(\frac{\delta Q}{T}\right)_C$$

As path C was arbitrary, the general result is

$$dS \geq \frac{\delta Q}{T}$$

or $$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

In these equations the equality holds for a reversible process and the inequality for an irreversible process.

- Thus, If an amount of heat δQ is transferred to a control mass at temperature T in a reversible process, the change of entropy is given by the relation.

$$dS = \left(\frac{\delta Q}{T}\right)_{rev}$$

- If any irreversible effects occur while the amount of heat δQ is transferred to the control mass at temperature T, however, the change of entropy will be greater than that of the reversible process. We would then write

$$dS > \left(\frac{\delta Q}{T}\right)_{irr}$$

Entropy Generation

The conclusion from the previous consideration is that the entropy change for an irreversible process is larger than the change in a reversible process for the same δQ and T. This can be written out in a common form as an equality

$$dS = \frac{\delta Q}{T} + \delta S_{gen}$$

Provided the last term is positive,

$$\delta S_{gen} \geq 0$$

The amount of entropy, δS_{gen}, is the entropy generation in the process due to irreversibilities occurring inside the system.

- This internal generation can be caused by the processes such as friction, unrestrained expansions, and the internal transfer of energy (redistribution) over a finite temperature difference.
- In addition to this internal entropy generation, external irreversibilities are possible by heat transfer over finite temperature differences as the δQ is transferred from a reservoir or by the mechanical transfer of work.
- We can generate but not destroy entropy. This is in contrast to energy which we can neither generate nor destroy.

- Since $\delta Q = 0$ for an adiabatic process, and the increase in entropy is always associated with the irreversibilities.
- The presence of irreversibilities will cause the actual work to be smaller than the reversible work. This means less work out in an expansion process and more work input in a compression process.

Principles of the increase of Entropy

Consider the process shown in Fig. 3.12 in which a quantity of heat δQ is transferred from the surroundings at temperature T_0 to the control mass at temperature T. Let the work done during this process be δW.

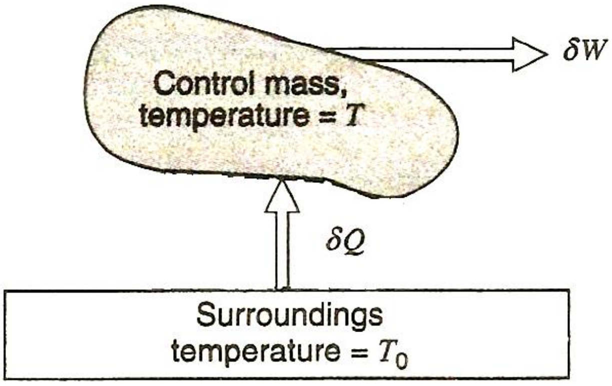


Fig. 3.12: Entropy Change for the Control Mass Plus Surroundings

For this process we can apply equation 3.38 to the control mass and write

$$\delta S_{c.m.} \geq \frac{\delta Q}{T}$$

For the surroundings at T_0, δQ is negative, and we assume a reversible heat extraction so

$$\delta S_{surr} = \frac{-\delta Q}{T_0}$$

The total net change of entropy is therefore

$$\delta S_{net} = dS_{c.m.} + dS_{surr} \geq \frac{\delta Q}{T} - \frac{\delta Q}{T_0}$$

$$\geq \delta Q \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

If T > T_0, the heat transfer is from the control mass to the surroundings, and both δQ and the quantity {(1/T) – (1/T_0)} are negative, thus yielding the same result.

$$dS_{net} = dS_{c.m.} + dS_{surr} \geq 0$$

The net entropy change could also be termed the total entropy generation:

$$dS_{net} = dS_{c.m.} + dS_{surr} = \sum \delta W_{gen} \geq 0$$

where the equality holds for reversible processes and the inequality for irreversible processes.

- This is a very important equation, not only for thermodynamics but also for philosophical thought. This equation is referred to as the principle of the increase of entropy.
- The great significance is that the only processes that can take place are those in which the net change in entropy of the control mass plus its surroundings increases (or in the limit, remain constant). The reverse process, in which both the control mass and surroundings are returned to their original state, can never be made to occur.

- Thus, the principle of the increase of entropy can be considered a quantitative general statement of the second law and applies to the combustion of fuel in our automobile engines, the cooling of our coffee, and the processes that take place in our body.

Entropy Change of a Solid or Liquid

Writing the first thermodynamic property relation,

$$Tds = du + Pdv$$

Since change in specific volume for a solid or liquid is very small,

$$ds \approx \frac{du}{T} \approx c\frac{dT}{T}$$

For many processes involving a solid or liquid, we may assume that the specific heat remains constant, in which case equation 3.47 can be integrated. The result is

$$s_2 - s_1 = c\ in\ \frac{T_2}{T_1}$$

Where, C is the specific heat in J/kg -K.

Entropy Change of an Ideal Gas

Writing the first thermodynamic property relation,

$$Tds = du + Pdv$$

For an ideal gas, du = C_v dT and $\frac{P}{T} = \frac{R}{V}$

Therefore, ds = $c_v\frac{dT}{T} + R\frac{dv}{V}$

Upon integration, we have

$$s_2 - s_1 = \int_1^2 c_v\frac{dT}{T} + R\ ln\ \frac{v_2}{v_1}$$

Where, c_v is the specific heat at constant volume in J/kg –K.

Similarly,

$$Tds = dh - vdP$$

For an ideal gas, dh = c_p dT and $\frac{v}{T} = \frac{R}{P}$

Therefore, ds = $c_p\frac{dT}{T} - R\frac{dP}{P}$

Upon integration, we have

$$s_2 - s_1 = \int_1^2 c_p\frac{dT}{T} - R\ ln\ \frac{P_2}{P_1}$$

Where, c_p is the specific heat at constant pressure in J/kg –K.

Entropy as a Rate Equation

$$\frac{dS}{\delta t} = \frac{1}{T}\frac{\delta Q}{\delta t} + \frac{\delta S_{gen}}{\delta t}$$

High and Low Grade Energy

High Grade Energy: High Grade Energy is the energy that can be completely transformed into shaft work without any loss and hence is fully utilizable. Examples are mechanical and electric work, water, wind and ideal power; kinetic energy of jets; animal and manual power.

Low Grade Energy: Low Grade Energy is the energy of which only a certain portion can be converted into mechanical work. Examples are heat or thermal energy; heat from nuclear fission or fusion; heat from combustion of fuels such as coal, wood, oil, etc.

Available and Unavailable Energy

- The portion of thermal energy input to a cyclic heat engine which gets converted into mechanical work is referred to as available energy.
- The portion of thermal energy which is not utilizable and is rejected to the sink (surroundings) is called unavailable energy.
- The terms exergy and anergy are synonymous with available energy and unavailable energy, respectively. Thus Energy = exergy+anergy.

The following two cases arise when considering available and unavailable portions of heat energy

Case 1: Heat is withdrawn at constant temperature

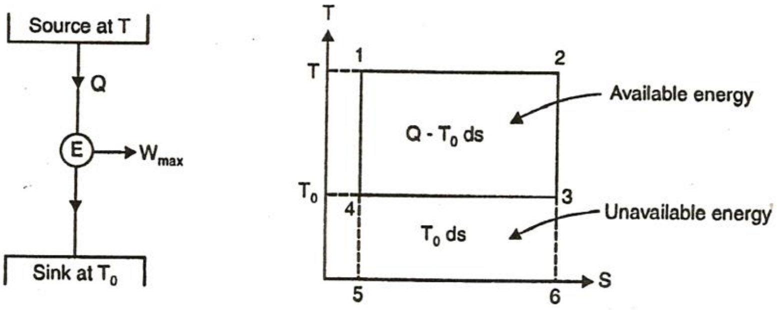


Fig. 3.13: Available and Unavailable Energy: Heat Withdrawn from an Infinite Reservoir

Fig.3.13 represents a reversible engine that operates between a constant temperature reservoir at temperature T and a sink at temperature T_0. Corresponding to heat Q supplied by the reservoir, the available work W_{max} is given by

$$\eta = \frac{W_{max}}{Q} = \frac{T-T_0}{T}$$

Therefore,

W_{max} = Available energy = $Q\left[\frac{T-T_0}{T}\right] = Q\left[1-\frac{T_0}{T}\right] = Q - T_0\frac{Q}{T} = Q - T_0\,ds$

Unavailable energy = $T_0\,ds$

Where ds represents the change of entropy of the system during the process of heat supply Q.

Case 2: Heat is withdrawn at varying temperature.

In case of a finite reservoir, the temperature changes as heat is withdrawn from it (Fig. 3.14), and as such the supply of heat to the engine is at varying temperature. The analysis is then made by breaking the process into a series of infinitesimal Carnot cycles each supplying δQ of heat at the temperature T (different for each cycle) and rejecting heat at the constant temperature T_0. Maximum amount of work (available energy) then equals

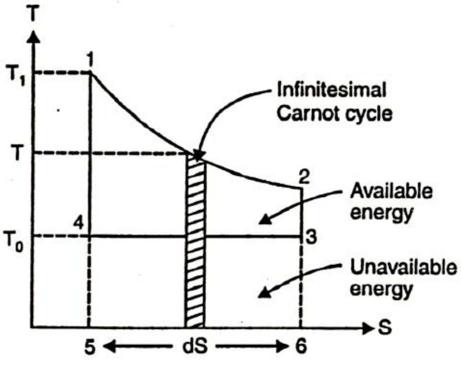


Fig. 3.14: Available and Unavailable Energy: Heat Supply at varying Temperature

$$\begin{aligned} W_{max} &= \int \left[1-\frac{T_0}{T}\right]\delta Q \\ &= \int \delta Q - \int T_0 \frac{\delta Q}{T} \\ &= \int \delta Q - T_0 \int \frac{\delta Q}{T} = Q - T_0\, ds \end{aligned}$$

It is to be seen that expressions for both the available and unavailable parts are identical in the two cases.

Loss of Available Energy due to Heat Transfer through a Finite Temperature Difference

Consider a certain quantity of heat Q transferred from a system at constant temperature T_1 to another system at constant temperature T_2 ($T_1>T_2$) as shown in Fig. 3.15.

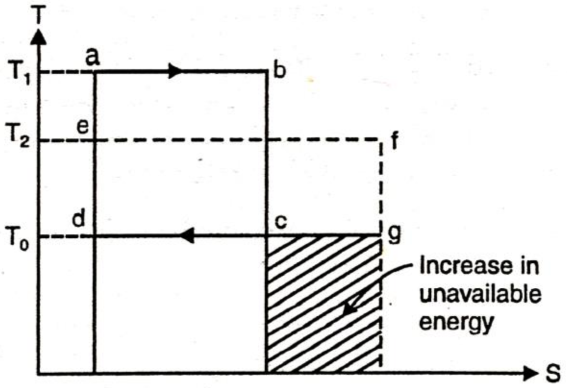


Fig. 3.15: Decrease in Available Energy due to Heat Transfer through a Finite Temperature Difference

Before heat is transferred, the energy Q is available at T_1 and the ambient temperature is T_0.

Therefore, Initial available energy, $(AE)_1 = Q\left[1-\frac{T_0}{T_1}\right]$

After heat transfer, the energy Q is available at T_2 and again the ambient temperature is T_0. Therefore, Final available energy, $(AE)_2 = Q\left[1-\frac{T_0}{T_2}\right]$

Change in available energy = $(AE)_1-(AE)_2 = Q\left[1-\frac{T_0}{T_1}\right]-Q\left[1-\frac{T_0}{T_2}\right]$

$$= T_0\left[\frac{-Q}{T_1}+\frac{Q}{T_2}\right] = T_0(dS_1+dS_2) = T_0(dS)_{net}$$

Where $dS_1 = -\frac{Q}{T_1}$, $dS_2 = \frac{Q}{T_2}$ and $(dS)_{net}$ is the net change in the entropy of the combination to the two interacting systems. This net entropy change is called the entropy change of universe or entropy production.

Since the heat transfer has been through a finite temperature difference, the process is irreversible, i.e., $(dS)_{net}>0$ and hence there is loss or decrease of available energy.

The above aspects lead us to conclude that:

- Whenever heat is transferred through a finite temperature difference, there is always a loss of available energy.
- Greater the temperature difference (T_1-T_2), the more net increase in entropy and, therefore, more is the loss of available energy.
- The available energy of a system at a higher temperature is more than at a lower temperature, and decreases progressively as the temperature falls.

- The concept of available energy provides a useful measure of the quality of energy. Energy is said to be degraded each time it flows through a finite temperature difference. The second law may, therefore, be referred to as law of degradation of energy.

Availability

- The work potential of a system relative to its dead state, which exchanges heat solely with the environment, is called the *availability* of the system at that state.
- When a system and its environment are in equilibrium with each other, the system is said to be in its dead state.
- Specifically, a system in a dead state is in thermal and mechanical equilibrium with the environment at T_0 and P_0.
- The numerical values of (T_0, P_0) recommended for the dead state are those of the standard atmosphere, namely, 298.15 K and 1.01325 bars (1 atm).

Availability of Non-flow or Closed System

Consider a piston-cylinder arrangement (closed system) in which the fluid at P_1, V_1, T_1, expands reversibly to the environmental state with parameters P_0, V_0, T_0. The following energy (work and het) interactions take place:

- The fluid expands and expansion work W_{exp} is obtained. From the principle of energy conservation, $\delta Q = \delta W + dU, we\ get: \ -Q = W_{exp} + (U_0 - U_1)$

  The heat interaction is negative as it leaves the system.

  Therefore $W_{exp} = (U_1 - U_0) - Q$

- The heat Q rejected by the piston-cylinder assembly may be made to run a reversible heat engine. The output from the reversible engine equals

  $W_{eng} = Q\left[1 - \frac{T_0}{T_1}\right] = Q - T_0(S_1 - S_0)$ **(Equ.3.60)**

The sum total of expansion work W_{exp} and the engine work W_{eng} gives maximum work obtainable from the arrangement.

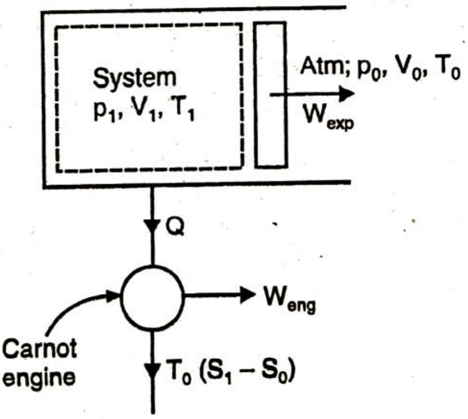


Fig. 3.16: Availability of a Non-Flow System

$$W_{max} = [(U_1 - U_0) - Q] + [Q - T_0(S_1 - S_0)]$$
$$= (U_1 - U_0) - T_0(S_1 - S_0)$$

The piston moving outwards has to spend a work in pushing the atmosphere against its own pressure. This work, which may be called as the surrounding work is simply dissipated, and as such is not useful. It is given by

$$W_{surr} = P_0(V_0 - V_1)$$

The energy available for work transfer less the work absorbed in moving the environment is called the useful work or net work.

Therefore, Maximum available useful work or net work,

$$(W_{useful})_{max} = W_{max} - W_{surr}$$
$$= (U_1 - U_0) - T_0(S_1 - S_0) - P_0(V_0 - V_1)$$
$$= (U_1 + P_0V_1 - T_0S_1) - (U_0 + P_0V_0 - T_0S_0)$$
$$= A_1 - A_0$$

Where $A = (U+P_0V - T_0S)$ is known as non-flow availability function. It is a composite property of the system and surroundings as it consists of three extensive properties of the system (U, V and S) and two intensive properties of the surroundings (P_0 and T_0).

When the system undergoes a change from state 1 to state 2 without reaching the dead state, then

$$(W_{useful})_{max} = W_{net} = (A_1 - A_0) - (A_2 - A_0) = A_1 - A_2$$

Availability of Steady Flow System

Consider a steady flow system and let it be assumed that the following fluid has the following properties and characteristics:

Internal energy U, specific volume V, specific enthalpy H, pressure P, velocity C and location Z.

The properties of the fluid would change when flowing through the system. Let subscript 1 indicate the properties of the system at inlet and subscript 0 be used to designate the fluid parameters at outlet corresponding to dead state. Further let Q units of heat be rejected by the system and let the system deliver W_{shaft} units of work.

$$U_1 + P_1V_1 + \frac{C_1^2}{2} + gZ_1 - Q = U_0 + P_0V_0 + \frac{C_0^2}{2} + gZ_0 + W_{shaft}$$

Neglecting potential and kinetic energy changes,

$$U_1 + P_1V_1 - Q = U_0 + P_0V_0 + W_{shaft}$$
$$H_1 - Q + H_0 + W_{shaft}$$

Therefore, Shaft work $W_{shaft} = (H_1 - H_0) - Q$

The heat Q rejected by the system may be made to run a reversible heat engine. The output from this engine equals

$W_{eng} = Q\left[1 - \frac{T_0}{T_1}\right] = Q - T_0(S_1 - S_0)$ **(Equation 3.67)**

Therefore, Maximum available useful work or net work

$W_{net} = W_s + W_{eng} = (H_1 - H_0) - Q + Q - T_0(S_1 - S_0)$

$= (H_1 - T_0 S_1) - (H_0 - T_0 S_0)$

$= B_1 - B_0$ **(Equation 3.68)**

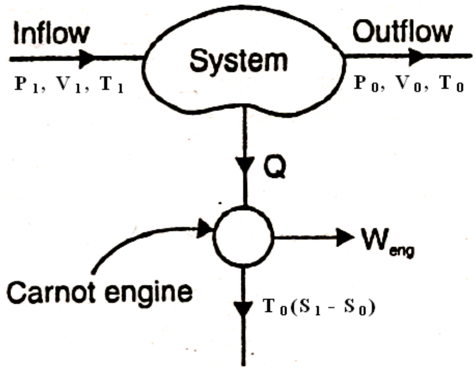


Fig. 3.17: Availability of a Steady flow System

Where $B = (H - T_0S)$ is known as the steady flow availability function. It is composite property of system and surroundings involving two extensive properties H and S of the system and one intensive property T_0 of the surroundings.

When the system changes from state 1 to some intermediate state 2, the change in steady flow availability function is given by

$$dB = (B_1 - B_0) - (B_2 - B_0) = B_1 - B_2$$

Helmholtz and Gibb's Functions

For a non-flow process, the maximum work output from the system when $T_1 = T_2 = T_0$, is given by

$$W_{max} = (U_1 - T_1S_1) - (U_2 - T_2S_2) = A_1 - A_2$$

- The term (U – TS) is called the Helmholtz function and is defined as the difference between the internal energy and the product of temperature and entropy.
- The maximum work of the process is equal to the decrease in Helmholtz function of the system.

In the case of flow process, the maximum work output from the system when $T_1 = T_2 = T_0$ and neglecting kinetic and potential energies, is given by

$$\begin{aligned} W_{max} &= (U_1 + P_1V_1 - T_1S_1) - (U_2 + P_2V_2 - T_2S_2) \\ &= (H_1 - T_1S_1) - (H_2 - T_2 S_2) = G_1 - G_2 \end{aligned}$$

- The term (H – TS) is called Gibb's function and is defined as the difference between enthalpy and product of temperature and entropy.
- The changes of both Helmholtz and Gibb's functions are called free energy i.e., energy that is free to be converted into work. Further, both the Helmholtz and Gibb's functions establish a criterion for thermodynamic equilibrium. At equilibrium, these functions are at their minimum values.

Maxwell Relations

The Maxwell relations can be derived from the different forms of the thermodynamic property relations discussed earlier such as

$du = Tds - Pdv$; $dh = Tds + vdP$;

$A = U - TS$ (or) $a = u - Ts$ and $G = H - TS$ (or) $g = h - Ts$

These relations are exact differentials and are of the general form $dz = M\,dx + N\,dy$.

For exact differentials, we have

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

Therefore using this relationship we can derive the following equations:

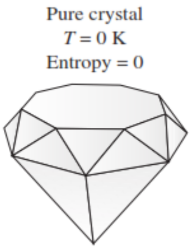
$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad ; \quad \left(\frac{\partial T}{\partial P}\right)_s = -\left(\frac{\partial v}{\partial s}\right)_P$$

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

These four equations are known as the Maxwell Relations for a simple compressible fluid.

Third Law of Thermodynamics (Nernst Law)

At absolute zero temperature, the entropy of all homogeneous crystalline (condensed) substances in a state of equilibrium becomes zero. the molecules of a substance in solid phase continually oscillate, creating an uncertainty about their position. These oscillations, however, fade as the temperature is decreased, and the molecules supposedly become motionless at absolute zero. This represents a state of ultimate molecular order (and minimum energy). Therefore, *the entropy of a pure crystalline substance at absolute zero temperature is zero* since there is no uncertainty about the state of the molecules at that instant. This statement is known as the **third law of thermodynamics**. The third law of thermodynamics provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is called **absolute entropy**, and it is extremely useful in the thermodynamic analysis of chemical reactions. Notice that the entropy of a substance that is not pure crystalline (such as a solid solution) is not zero at absolute zero temperature. This is because more than one molecular configuration exists for such substances, which introduces some uncertainty about the microscopic state of the substance.



ENGINEERING THERMODYNAMICS

Unit – IV

Objectives:

- To introduce the students to Properties of Pure substances, various Phase diagram like P-v, P-T, T-s and h-s and steam tables.

Syllabus:

Pure substance, phase, phase transformation, P-V, P-T, T-S and h-s diagrams of a pure substance (water), Triple point, critical point, P-V-T surface, Dryness fraction, steam tables, Mollier diagram, Determination of steam Properties using steam tables and mollier chart, Various Thermodynamic Processes, and energy transfer, measurement of steam quality- Steam calorimetry, clausius- clapeyron equation,

Outcomes:

Students will be able to

- Evaluate properties of substances at saturation points, at mixtures of phases and Draw phase diagram (P-V, P-T, T-S and h-s) of substances.
- Define triple point, critical point, Dryness fraction.
- Analyse heat and work quantities by using steam tables and Mollier chart.
- Evaluate quality of steam by using Various steam calorimeters.
- Evaluate Latent heat by using Phase transformations using Clausius- clapeyron equation.

UNIT IV

PROPERTIES OF PURE SUBSTANCES

4.1 Pure substance

- A ***Pure substance*** is a substance of constant chemical composition throughout its mass. It is a one component system and it may exist in one or more phases.

  Or

  A substance that has a fixed chemical composition throughout is called a Pure substance. Water, nitrogen, helium, and carbon dioxide, for example are all ***pure substances***.

- A pure substance does not have to be of a single chemical element or compound. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous.
  Air for example, is a mixture of several gases, but is often considered to be pure substance because it has a uniform chemical composition. However a mixture of oil and water is not a pure substance. Since oil is not soluble in water, it will collect on top of water, forming two chemically dissimilar regions.

- **A mixture of two or more phases of a pure substance** is still a pure substance as long as the chemical composition of all the phases is same.
  A mixture of ice, liquid water for example is a pure substance because both phases have the same chemical composition.

- A mixture of liquid air and gaseous air is ***not*** a pure substance since the composition of liquid air is different from the composition of gaseous air, and the mixture is no longer chemically homogeneous.

We know that substance exists in different phases. At room temperature and pressure, copper is a solid, mercury is a liquid, and nitrogen is a gas. Under different conditions each may appear in different phase. Even though there are three principle phases- solid, liquid, and gas- a substance may have several phases within a principle phase, each with a different molecular structure. For example carbon may exist as diamond, graphite in solid phase. Helium has two liquid phases; Iron has three solid phases. Ice may exist at seven different phases at high pressures.

- A ***phase*** is identified as having a distinct molecular arrangement that is homogeneous throughout and separated from others by easily identifiable boundary surfaces.

- Intermolecular bonds are strongest in solids, and weakest in gases. One reason is that molecules in solid are closely packed together, where as in gases they are separated by relatively large distances.

- The molecules in a solid are arranged in a three – dimensional pattern (lattice) that is repeated throughout. Because of the small distances between the molecules in a solid, the attractive forces of molecules on each other are large and keep the molecules in fixed positions. The attractive forces between the molecules turn to repulsive forces as the distance between the molecules approaches to zero, thus preventing the molecules from piling up on top of each other. Even though the molecules in a solid cannot move relative to each other, they continuously oscillate about their equilibrium positions. The velocity of the molecules during these oscillations depends on the temperature. At sufficiently high temperatures, the velocity of the molecules may reach a point where the intermolecular forces are partially overcome and groups of molecules break away. This is the beginning of ***Melting (change of Phase from*** Solid ***to Liquid) process.***

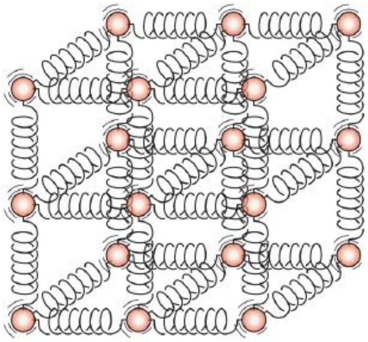
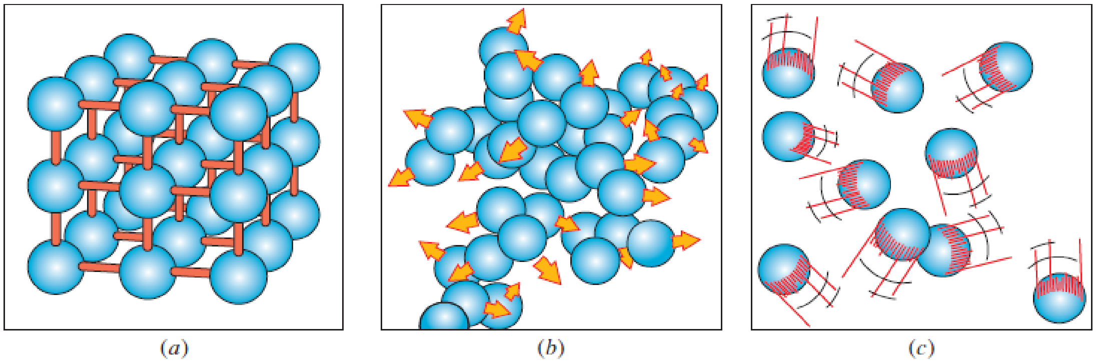


Fig. 4.1 The molecules in a solid are kept at their positions by the large spring like intermolecular forces.

- The molecular spacing in the ***liquid phase*** is not much different from that of solid phase, except the molecules are no longer at fixed positions relative to each other and they can rotate and translate freely. In liquids the intermolecular forces are weaker relative to solid, but still relatively strong compared with gases.

- In the ***gas phase*** the molecules are far apart each other, and molecular order is nonexistent.


(a) (b) (c)

The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

4.2 *Phase change process of pure substance*

There are many practical situations where two phases of a pure substance coexist in equilibrium. Water exists as a mixture of liquid and vapor in the boiler and condenser of a steam power plant. The refrigerant turns from liquid to vapor in the freezer of a refrigerator.
As a familiar substance water is used to demonstrate the basic principles involved.

Compressed liquid and saturated liquid

Consider a piston cylinder device containing liquid water at 20^0C and 1 atm. Pressure (fig. 4.2 a). let this is state 1.Under these conditions, water exists in the liquid phase, and it is called a ***compressed liquid*** or a ***sub cooled liquid***, meaning that it is not about to vaporize. Heat is now transferred to water until its temperature rises to say 40^0C. As the temperature rises, the liquid water expands slightly, and so its specific volume increases. To accommodate this expansion, the piston moves up slightly. The pressure in the cycle remains constant at 1 atm during this process. Water is still a compressed liquid at this state since it has not started to vaporize.

As more heat is transferred, the temperature is keeps rising until it reaches say 100^{0}C (fig.4.2 b). Let this is state 2. At this point water is still a liquid but any heat addition will cause some of the liquid to vaporize. That is a phase change process from liquid to vapor is about to takes place. A liquid is about to vaporize is called saturated liquid. Therefore state 2 is a ***saturated liquid state***.

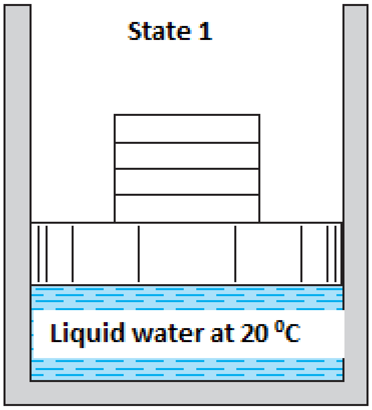


Fig. 4.2 a

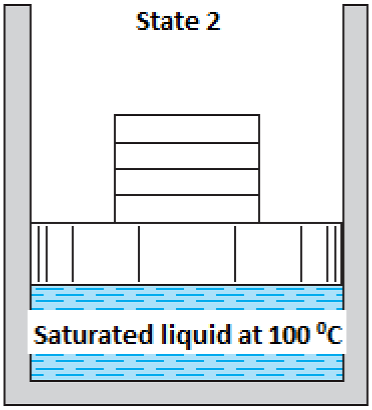


Fig 4.2b

- ***Saturated vapor and super heated vapor***

Once boiling starts, the temperature stops rising until the liquid is completely vaporized. That is, the temperature will remains constant during the entire phase-change process if the pressure is held constant. During the boiling process, the only change we will observe is a large increase in volume and a steady decline in the liquid level as a result of more liquid turning to vapor.

Mid way about complete vaporization, the cylinder contains equal amounts of liquid and vapor (fig. 4.2 c). Let this is at state 3. As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized. At this point the entire cylinder is filled with vapor (fig 4.2 d). Let this is state 4. Any heat loss from this vapor will cause some of the vapor to condense (phase change from vapor to liquid). A vapor that is about to condense is called ***Saturated Vapor***.

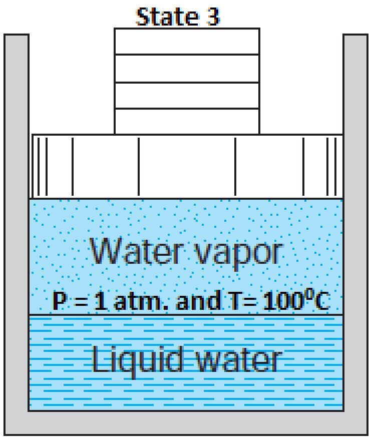


Fig. 4.2 c

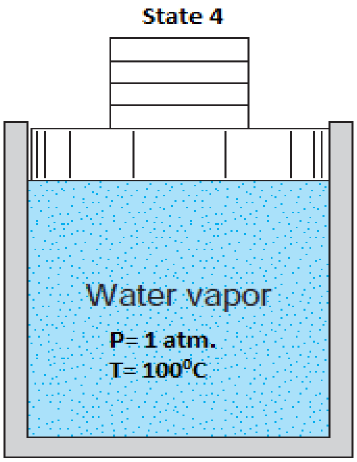


Fig.4.2 d

Therefore state 4 is a saturated vapor state. A substance at states between 2 and 4 is referred to as a saturated liquid- vapor mixture since liquid and vapor phases coexists in equilibrium at these states.

Once the phase change process is completed, we are back to single phase region again (this time vapor phase) and further transfer of heat results in an increase in both the temperature and the specific volume. At state 5, the temperature of the vapor is let us say 300^{0}C (fig. 4.2e), and if we transfer some heat from vapor, the temperature may drop somewhat but no condensation will takes place as long as the temperature above 100^{0}C (for p=1atm). A vapor that is not about to condense (i.e not saturated vapor) is called a ***super heated vapor***. [see T-υ diagram of water at constant pressure, Fig. 4.2f]

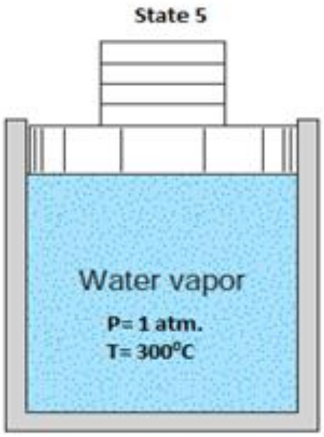


Fig.4.2 e

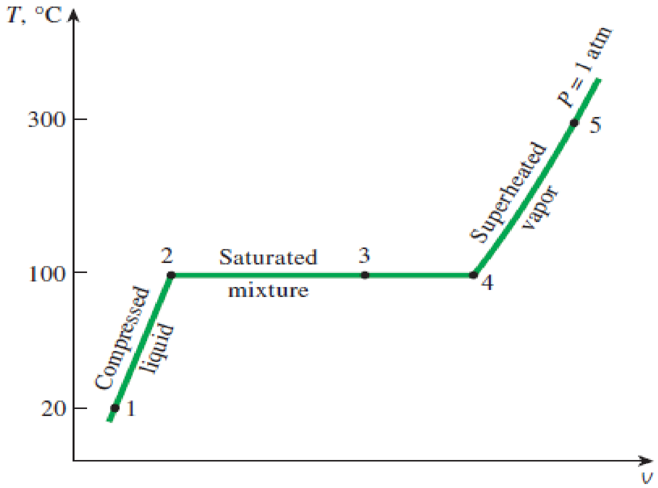


Fig.4.2 f T-υ diagram for the heating process of water at constant pressure of 1 atm

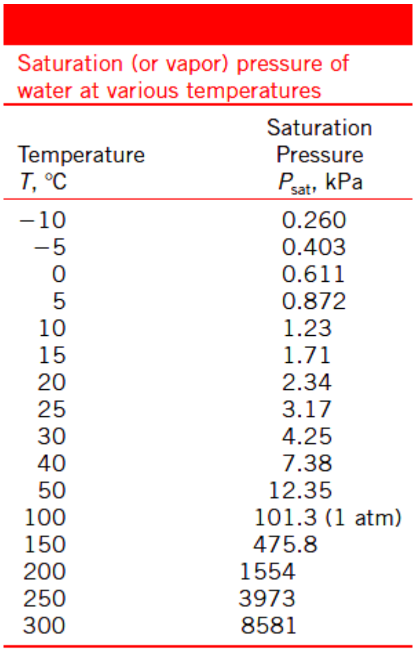
4.3 Saturation Temperature and saturation Pressure:

The statement “water boils at 100^{0}C” is incorrect. The correct statement is “water boils at 100^{0}C at 1 atm pressure.” The only reason water started boiling at 100^{0}C was because we held the pressure constant at 1 atm (101.325 kPa). If the pressure inside the cylinder were raised to 500 kPa by adding weights on top of the piston, water would start boiling at 151.8^{0}C. That is, the temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.

- At a given pressure, the temperature at which a pure substance changes phase is called the ***saturation temperature*** T_{sat}. Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the ***saturation pressure*** P_{sat}. At a pressure of 101.325 kPa, T_{sat} is 99.97^{0}C.

  Conversely, at a temperature of 99.97^{0}C, P_{sat} is 101.325 kPa.

- Saturation tables that list the saturation pressure against the temperature (or the saturation temperature against the pressure) are available for practically all substances. A partial listing of such a table is given for water.



Saturation (or vapor) pressure of water at various temperatures

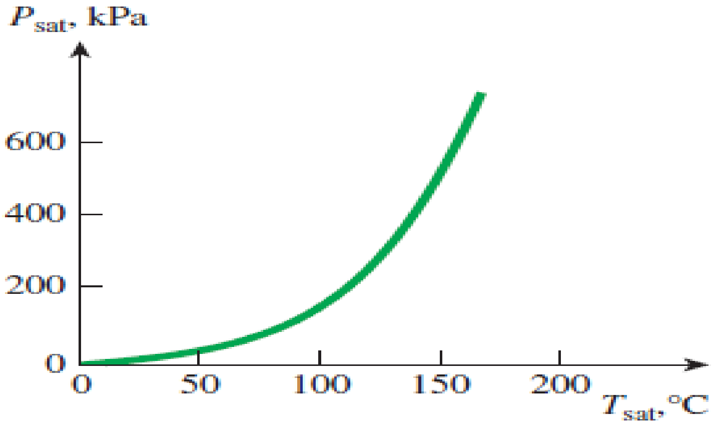
Temperature T, °C	Saturation Pressure P_{sat}, kPa
−10	0.260
−5	0.403
0	0.611
5	0.872
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.38
50	12.35
100	101.3 (1 atm)
150	475.8
200	1554
250	3973
300	8581

- This table indicates that the pressure of water changing phase (boiling or condensing) at 25°C must be 3.17 kPa, and the pressure of water must be maintained at 3976 kPa (about 40 atm) to have it boil at 250°C. Also, water can be frozen by dropping its pressure below 0.61 kPa.

- It takes a large amount of energy to melt a solid or vaporize a liquid. The amount of energy absorbed or released during a phase-change process is called the ***latent heat***. More specifically, the amount of energy absorbed during melting is called the ***latent heat of fusion*** and is equivalent to the amount of energy released during freezing.

- Similarly, the amount of energy absorbed during vaporization is called the ***latent heat of vaporization*** and is equivalent to the energy released during condensation. The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs. At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

- During a phase-change process, pressure and temperature are obviously dependent properties, and there is a definite relation between them, that is, $T_{sat} = f(P_{sat})$. A plot of T_{sat} versus P_{sat}, such as the one given for water in the following fig. 4.3 is called a ***liquid–vapor saturation curve***. A curve of this kind is characteristic of all pure substances.



The liquid - vapor saturation curve of a pure substance

Fig. 4.3

- From the figure it is clear that T_{sat} increases with P_{sat}. Thus, a substance at higher pressures boils at higher temperatures. In the kitchen, higher boiling temperatures mean shorter cooking times and energy savings.

4.4 Property Diagrams for Phase – change processes

4.4.1 The T-v diagram

- The phase-change process of water at 1 atm pressure was described in detail in section 4.2 and the plot on T-v diagram in Fig. 4.2f. Now we repeat this process at different pressures to develop the T-v diagram.

- Let us add weights on top of the piston until the pressure inside the cylinder reaches 10bar. At this pressure, water has a somewhat smaller specific volume than it does at 1 atm pressure. As heat is transferred to the water at this new pressure, the process follows a path that looks very much like the process path at 1 atm pressure, as shown in Fig. 4.4, but there are some noticeable differences.

- First, water starts boiling at a much higher temperature (179.9^{0}C) at this pressure. Second, the specific volume of the saturated liquid is larger and the specific volume of the saturated vapor is smaller than the corresponding values at 1 atm pressure. That is, the horizontal line that connects the saturated liquid and saturated vapor states is much shorter.

- As the pressure is increased further, this saturation line continues to shrink, as shown in Fig. 4.4, and it becomes a point when the pressure reaches 220.6 bar for the case of water. This point is called the ***critical point***, and it is defined as the point at which the saturated liquid and saturated vapor states are identical.

- The temperature, pressure, and specific volume of a substance at the critical point are called, respectively, the ***critical temperature*** T_{cr}, ***critical pressure*** P_{cr}, and ***critical specific volume*** v_{cr}. The critical-point properties of water are $P_{cr} = 220.6$bar , $T_{cr} = 373.95^{0}$C, and $v_{cr} = 0.003106$ m^3/kg. For helium, they are 2.3 bar, -267.85^{0}C, and 0.01444 m^3/kg.

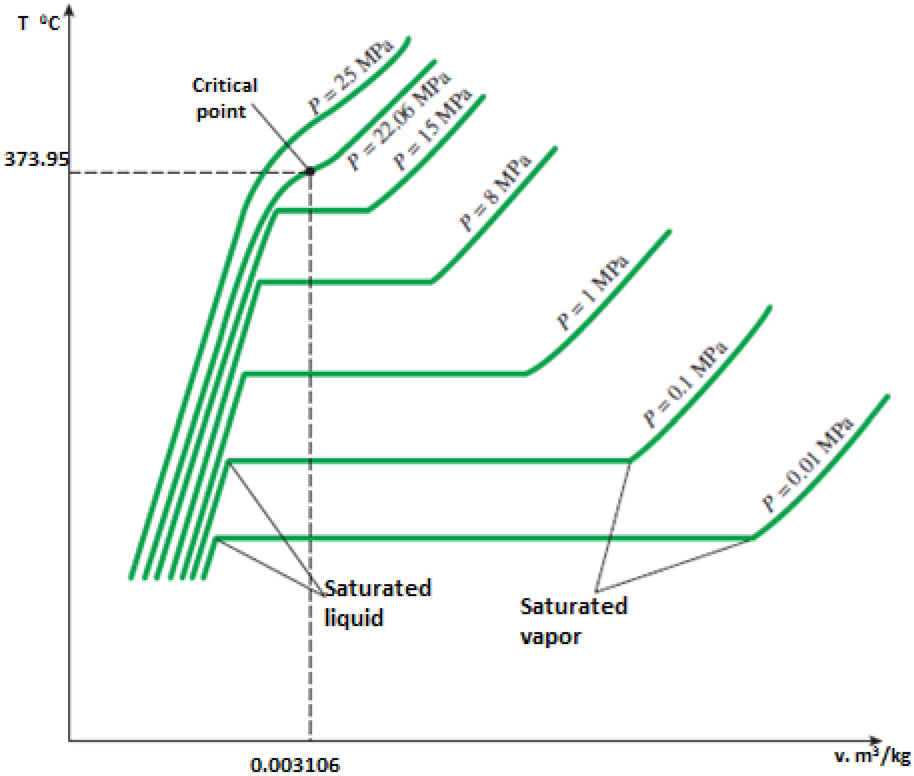


Fig.4.4 T-v diagram of constant pressure phase- change processes of pure substances at various pressures.

- At pressures above the critical pressure, there is not a distinct phase change process (Fig. 4.4a). Instead, the specific volume of the substance continually increases, and at all times there is only one phase present. Eventually, it resembles a vapor, but we can never tell when the change has occurred. Above the critical state, there is no line that separates the compressed liquid region and the superheated vapor region. However, it is customary to refer to the substance as superheated vapor at temperatures above the critical temperature and as compressed liquid at temperatures below the critical temperature.

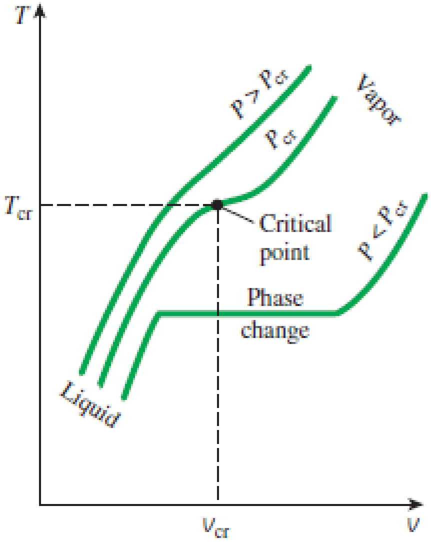


Fig 4.4 a, At pressures P>P$_{cr}$, there is no distinct phase change process.

- The saturated liquid states in Fig. 4.4 can be connected by a line called the ***saturated liquid line***, and saturated vapor states in the same figure can be connected by another line, called the ***saturated vapor line***. These two lines meet at the critical point, forming a dome as shown in Fig. 4.4b.

- All the compressed liquid states are located in the region to the left of the saturated liquid line, called the ***compressed liquid region***. All the superheated vapor states are located to the right of the saturated vapor line, called the ***superheated vapor region***. In these two regions, the substance exists in a single phase, a liquid or a vapor.

- All the states that involve both phases in equilibrium are located under the dome, called the ***saturated liquid–vapor mixture region***, or the ***wet region***.

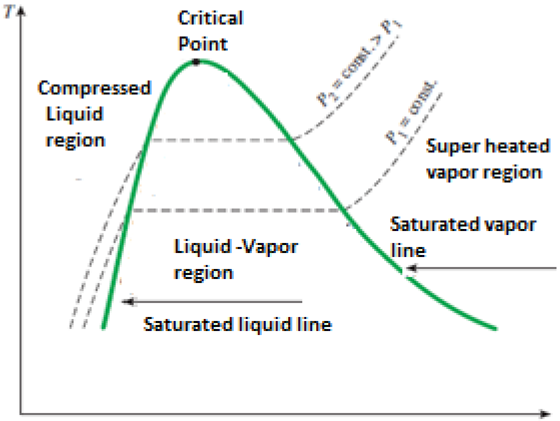


fig. 4.4b T-v diagram of pure substance

4.4.2 *The P-υ Diagram*

- Consider a unit mass of ice at -10^{0}C and 1atm contained in a piston-cylinder machine. Let the ice be heated slowly so that its temperature is always uniform.

  The changes which occur in the mass of water would be traced as the temperature is increased while the pressure is held constant. Let the state changes of water be plotted on p-υ coordinates. The distinct regimes of heating are as shown in following fig. 4.5a

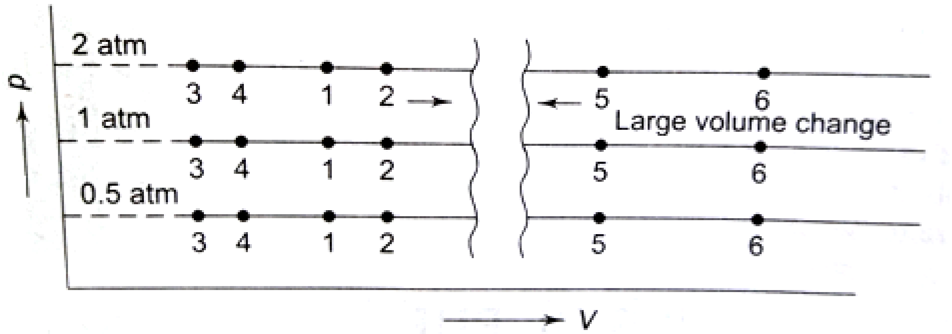
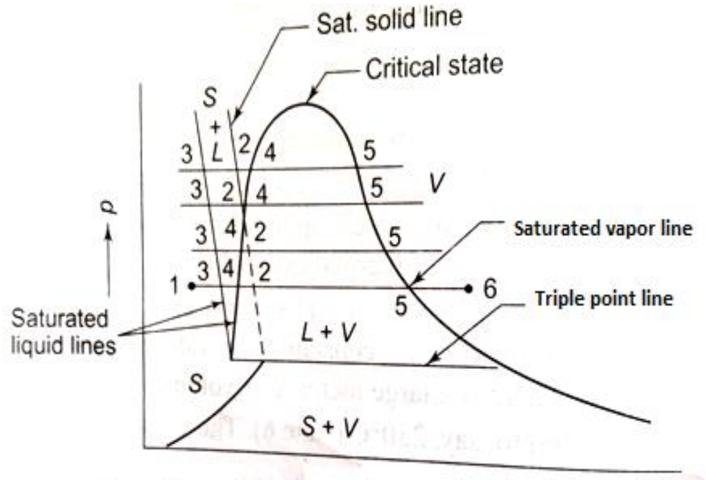


Fig.4.5a , Changes in the volume of water during heating at constant pressure

- 1-2 : The temperature of ice increase from -10^{0}C to to 0^{0}C. The volume of ice would increase. At state 2 i.e at 0^{0}C, the ice would start melting.
- 2-3 : Ice melts into water at constant temperature of 0^{0}C. At state 3 melting process ends. ***There is a decrease in volume which is peculiarity of water.***
- 3-4 : The temperature of water increases, upon heating from 0^{0}c to 100^{0}C. the volume of water increase because of thermal expansion.
- 4-5 : The water starts boiling at state 4 and boiling ends at state 5. This phase change from liquid to vapor occurs at a constant temperature of 100^{0}C. (the pressure is being constant at 1 atm). There is large increase in volume.
- 5-6 : The vapor is heated to say 250^{0}C (state 6) . The volume of vapor increases from υ_5 to υ_6.



4.5b, P-V diagram for substance that expands on freezing(water) → V

- Water existed in the solid phase between 1 and 2, in the liquid phase between 3 and 4, and in the gas phase beyond 5. Between 2 and 3, the solid changes into the liquid phase by absorbing the latent heat of fusion and between 4 and 5, the liquid changes into vapor phase by absorbing the latent heat of vaporization, both at constant temperature and pressure.

- The states 2, 3, 4, 5 are known as saturation states. A saturation state is a state from which a change of phase may occur without a change of pressure or temperature. State is a saturated solid state because a solid can change into liquid at constant pressure and temperature from state 2. States 3 and 4 are both saturated liquid states. In state 3, liquid is saturated with respect to solidification, where as in state 4, the liquid is saturated with respect to vaporization. State 5 is a saturated vapor state, because from state 5, the vapor can condense into liquid without a change of pressure or temperature.

- If the heating of ice at -10^{0}C to steam at 250^{0}C were done at constant pressure of 2 atm, similar regimes of heating would have been obtained with similar saturation states 2,3,4,5. (see Fig. 4.5 b for water and 4.5 c for any other substance)

- All saturated solid states 2 at various pressures are joined by a line and it is called ***saturated solid line.***

- Similarly, all the saturated liquid states 3 with respect to solidification, all the saturated liquid states 4 with respect to vaporization, and all the saturated vapor states 5 are joined together. The line passing through all the saturated liquid states 3 and 4 is known as saturated liquid line and the line passing through all the saturated vapor states 5, is the ***saturated vapor line.***

- The saturated liquid line with respect to vaporization and the saturated vapor line inclined towards each other and form a ***vapor dome***. The two lines meet at the ***critical state***.

- To the left of the saturated solid line is the solid region. Between the saturated solid line and saturated liquid line with respect to solidification, there exists a solid – liquid mixture (S+L) region. Between two saturated liquid lines is the compressed liquid region. The liquid – vapor mixture region (L+V) exists within vapor dome between the saturated liquid and saturated vapor lines. To the right of the saturated vapor region is the vapor region. The triple point is a line on the p-υ diagram where all the three phases' solid, liquid, and gas exist in equilibrium.

- At a pressure below the triple point line, the substance cannot exist in liquid phase, and the substance when heated, transforms from solid to vapor (known as sublimation) by absorbing the latent heat of sublimation from the surroundings. The region below the triple point line is therefore solid- vapor mixture region.

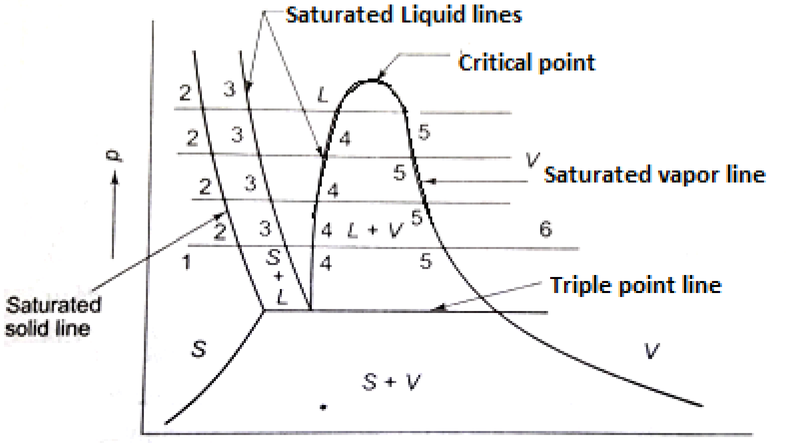
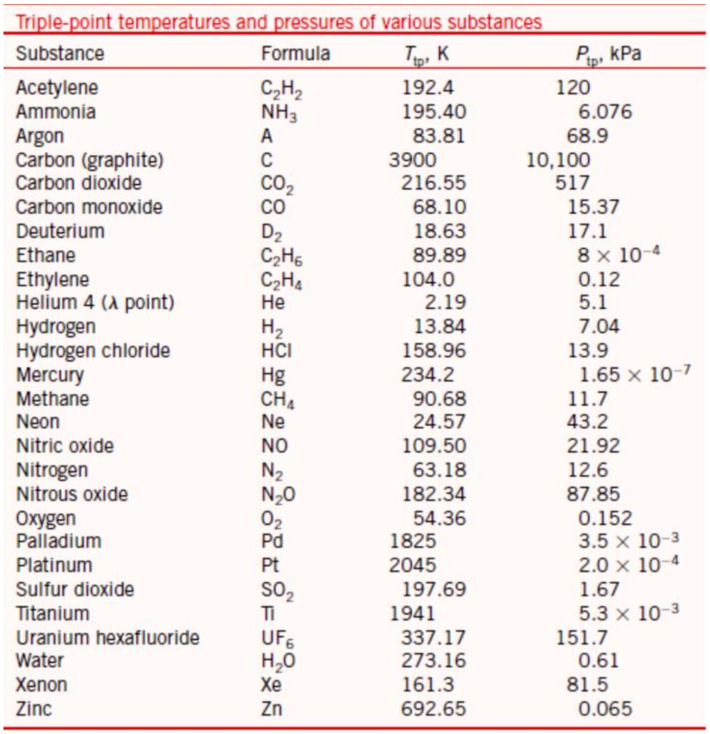


Fig.4.5 C, P-v Diagram for a substance other than water



Triple-point temperatures and pressures of various substances

Substance	Formula	T_{tp}, K	P_{tp}, kPa
Acetylene	C_2H_2	192.4	120
Ammonia	NH_3	195.40	6.076
Argon	A	83.81	68.9
Carbon (graphite)	C	3900	10,100
Carbon dioxide	CO_2	216.55	517
Carbon monoxide	CO	68.10	15.37
Deuterium	D_2	18.63	17.1
Ethane	C_2H_6	89.89	8×10^{-4}
Ethylene	C_2H_4	104.0	0.12
Helium 4 (λ point)	He	2.19	5.1
Hydrogen	H_2	13.84	7.04
Hydrogen chloride	HCl	158.96	13.9
Mercury	Hg	234.2	1.65×10^{-7}
Methane	CH_4	90.68	11.7
Neon	Ne	24.57	43.2
Nitric oxide	NO	109.50	21.92
Nitrogen	N_2	63.18	12.6
Nitrous oxide	N_2O	182.34	87.85
Oxygen	O_2	54.36	0.152
Palladium	Pd	1825	3.5×10^{-3}
Platinum	Pt	2045	2.0×10^{-4}
Sulfur dioxide	SO_2	197.69	1.67
Titanium	Ti	1941	5.3×10^{-3}
Uranium hexafluoride	UF_6	337.17	151.7
Water	H_2O	273.16	0.61
Xenon	Xe	161.3	81.5
Zinc	Zn	692.65	0.065

4.4.3 P-T diagram

- If the heating of ice at -10^{0}C to steam at 250^{0}C at the constant pressure of 1 atm is considered,

  1-2 is solid heating (ice), 2-3 is melting of ice at 0^{0}C, 3-4 is the liquid heating, 4-5 is the vaporization of water at 100^{0}C, and 5-6 is the heating in the vapor phase. The process will be reversed from state 6 to state 1 upon cooling. The curve passing through 2,3 is fusion curve, and the curve passing through 4,5 is called vaporization curve. If the vapor pressure of a solid is measured at different temperatures, and these are plotted, the sublimation curve will be obtained. (see Fig.4.6a and 4.6 b)
- The fusion curve, the vaporization curve and the sublimation curve meet at triple point.
- The slopes of the sublimation and vaporization curves for all substances are positive. The slope of fusion curve for most substances is positive, but for water it is negative.
- The temperature at which a liquid boils is very sensitive to pressure, as indicated by the vaporization curve which gives the saturation temperatures at different pressures, but the temperature at which a solid melts is not such a strong function of pressure, as indicated by the small slope of the fusion curve.

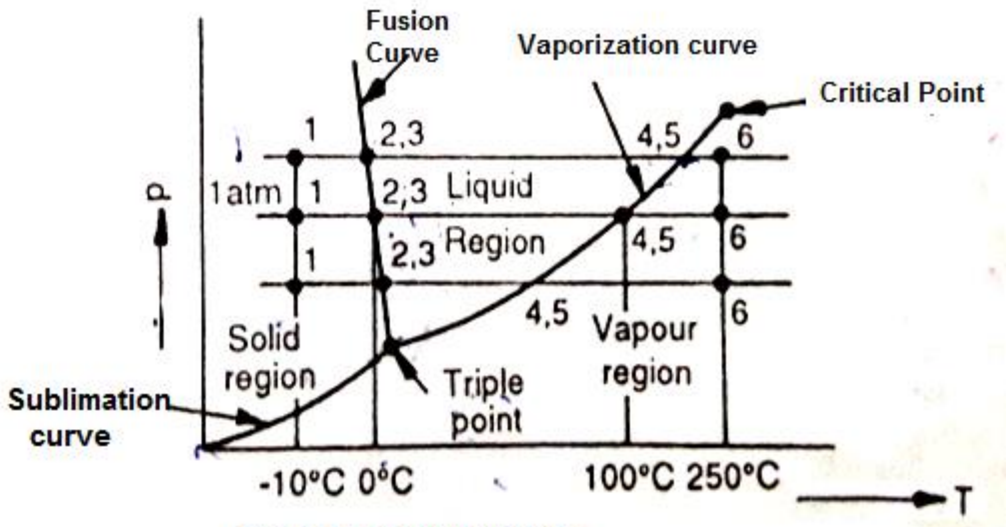
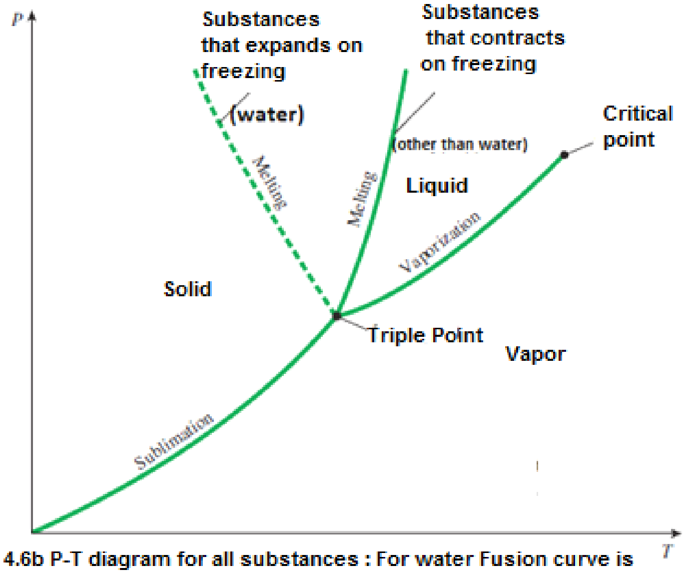


Fig.4.6 a, P-T diagram for water



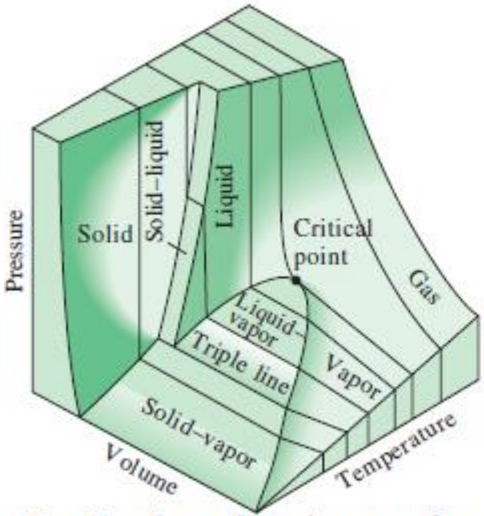
4.6b P-T diagram for all substances : For water Fusion curve is dotted line, other substances fusion curve is firm line

4.4.4 P-V-T Surface

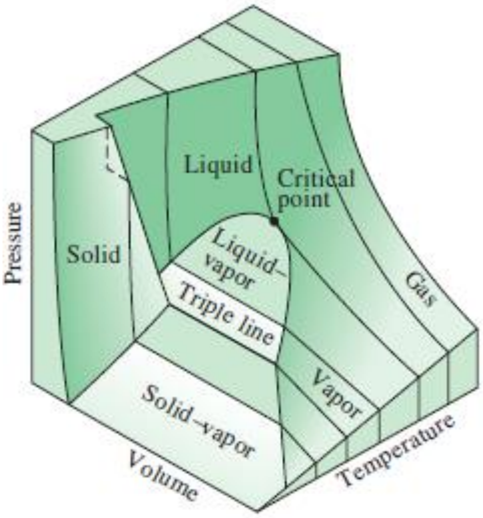
- All the points on the surface represent equilibrium states. All states along the path of a quasi-equilibrium process lie on the *P-v-T* surface since such a process must pass through equilibrium states. The single-phase regions appear as curved surfaces on the *P-v-T* surface, and the two-phase regions as surfaces perpendicular to the *P-T* plane. This is expected since the projections of two-phase regions on the *P-T* plane are lines.

- All the two-dimensional diagrams we have discussed so far are merely projections of this three-dimensional surface onto the appropriate planes .A

P-*v* diagram is just a projection of the *P*-*v*-*T* surface on the *P*-*v* plane, and a *T*-*v* diagram is nothing more than the bird's-eye view of this surface.

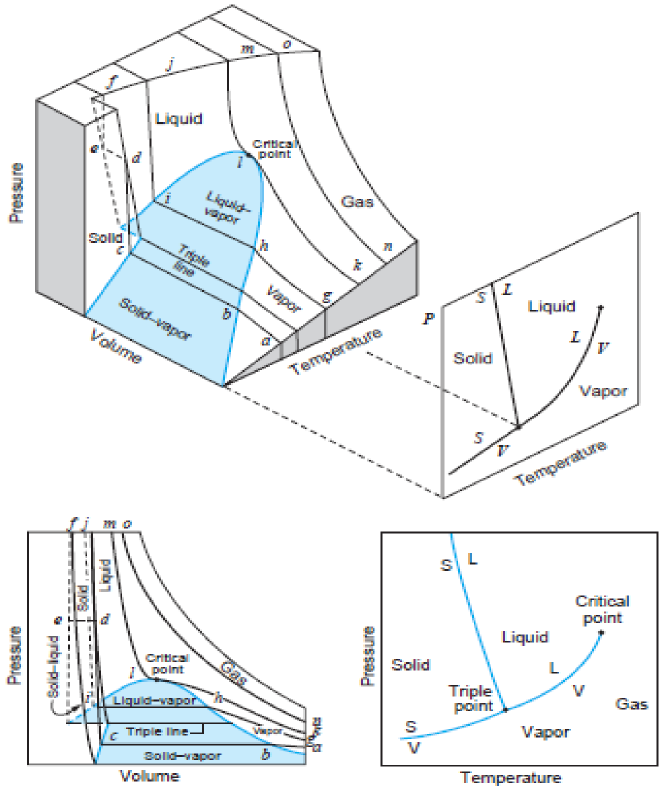


P-v-T surface of a substance that contracts on freezing.

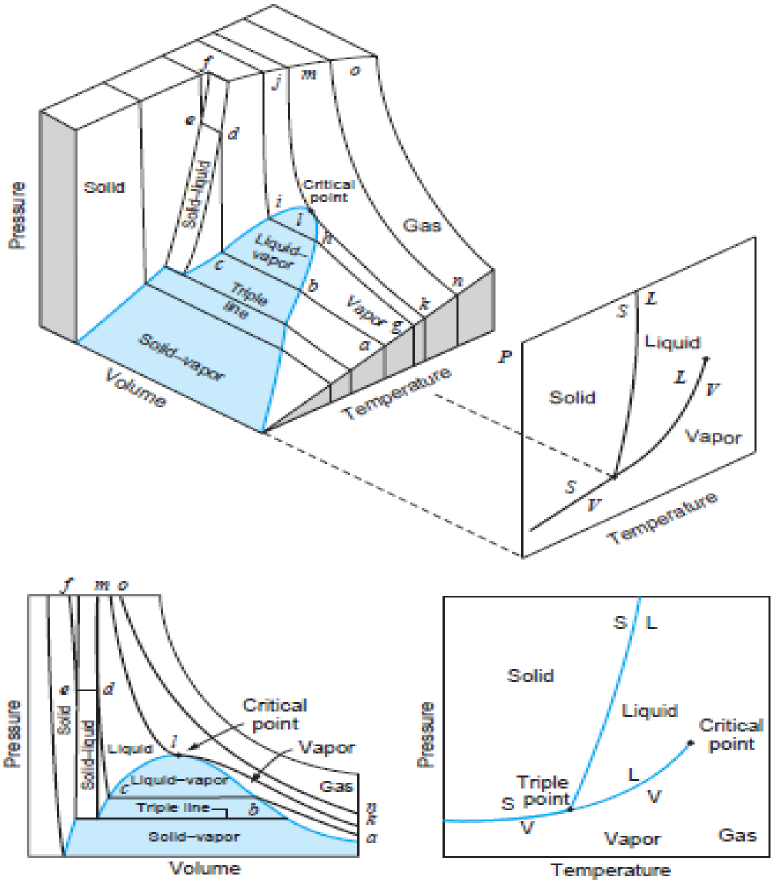


P-v-T surface of a substance that expands on freezing (water)

- ***Projections on planes***



P-V-T surface of a substance that expands on freezing



P-v-T surface of the substance that contracts on freezing

4.5 *T-S diagram*

- The heating of the system of 1kg of ice at -5^{0}C to steam at 250^{0}C is again considered, the pressure being maintained at 1 atm. The entropy increase of the system in different regimes of heating as flows.
- The entropy changes are shown in fir 4.8a. The curve 1-2-3-4-5-6 is the isobar of 1 atm. If during the heating process, the pressure had been maintained at 2 atm, a similar curve would be obtained.
- Most often liquid –vapor transformations only are of interest, and liquid, vapor, and the transition zones are shown in fig. 4.8b.

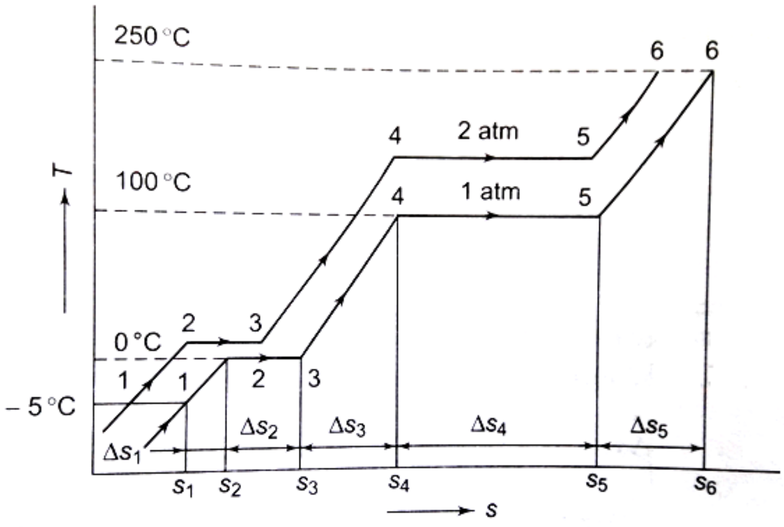


Fig.4.8 a *Isobars on T-s plot*

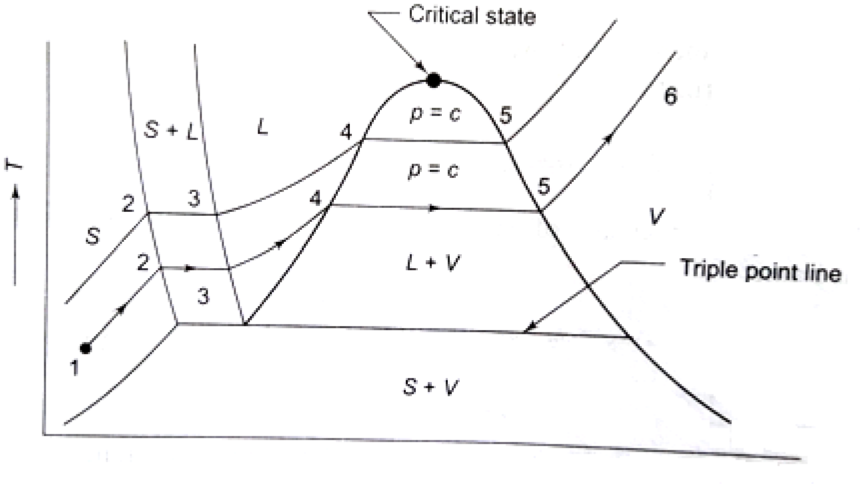


Fig. 4.8b, Phase diagram on T-S coordinates

4.6 *h-s Diagram*

- From the first and second laws of Thermodynamics, the following property relation was obtained.

$$Tds = dh - vdp$$

$$\left[\frac{\partial h}{\partial s}\right]_p = T$$

- This equation forms the basis of h-s diagram of pure substance, also called Mollier Diagram. The slope of isobar on h-s coordinates is equal to the saturation temperature (in Kelvin) at that pressure. If the temperature remains constant, the slope will remain constant. If the temperature increases, the slope of isobar will increase.

- Consider the heating of a system of ice at -5°C to steam at 250°C, the pressure being maintained at 1 atm. The slope of the isobar of 1 atm on the h-s coordinates (fig 4.9a) first increases as the temperature of ice increase from -5°C to 0°C (1-2). It's slope then remains constant as ice melts into water at the constant temperature of 0°C (2-3). The slope of isobar again increases as the temperature of water rises from 0°C to 100°C (3-4). The slope again remains constant as water vaporizes into steam at the constant temperature of 100°C (4-5). Finally the slope of isobar continues to increase as the temperature of the steam increases to 250°C (5-6) and beyond.

- Similarly isobars of different pressures can be drawn on the h-s diagram. Fig 4.9b shows phase diagram on h-s co-ordinates. Fig. 4.9 C shows h-s diagram for water.

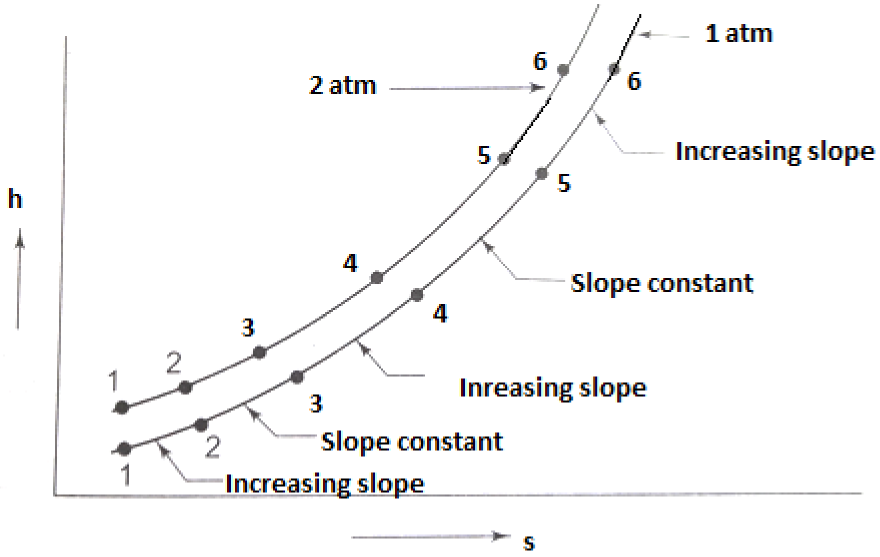


Fig. 4.9a Isobars on h-s Co-Ordinates

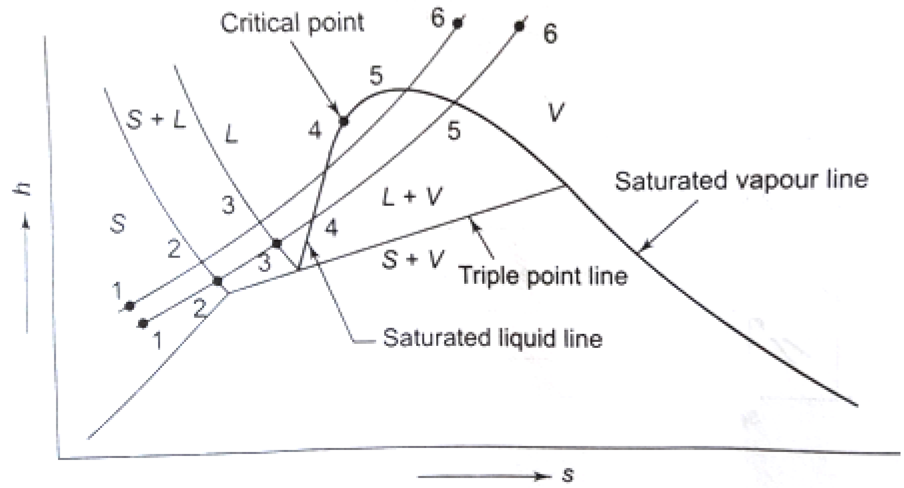


Fig. 4.9b Phase equilibrium diagram on h-s plot

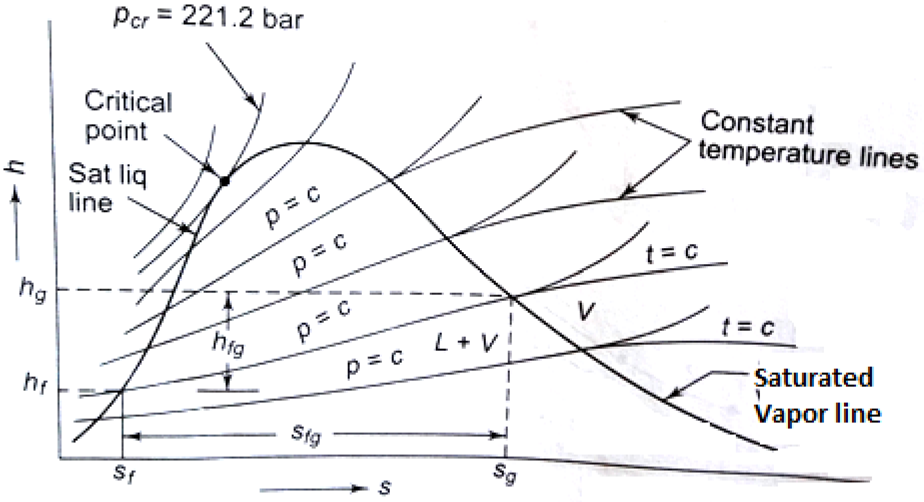


Fig. 4.9 C h-s diagram for water

4.7 Quality or dryness fraction

- For a two- phase liquid – vapor mixture, the ratio of mass of vapor present to the total mass of mixture is its quality. [See Fig 4.10].
- For saturated liquid x =0 and for dry saturated vapor x =1.
- In fig 4.10, m and n represents Saturated liquid (x=0) and saturated Vapor (x=1) states respectively. a,b,c represents constant dryness fraction lines corresponding to x=0.25, x=0.5, x=0.75 respectively.

$$x=\left[\frac{m_{vapor}}{m_{liquid}+m_{vapor}}\right]$$

Where m_{vapor} is the mass of vapor, and m_{liquid} is the mass of liquid.

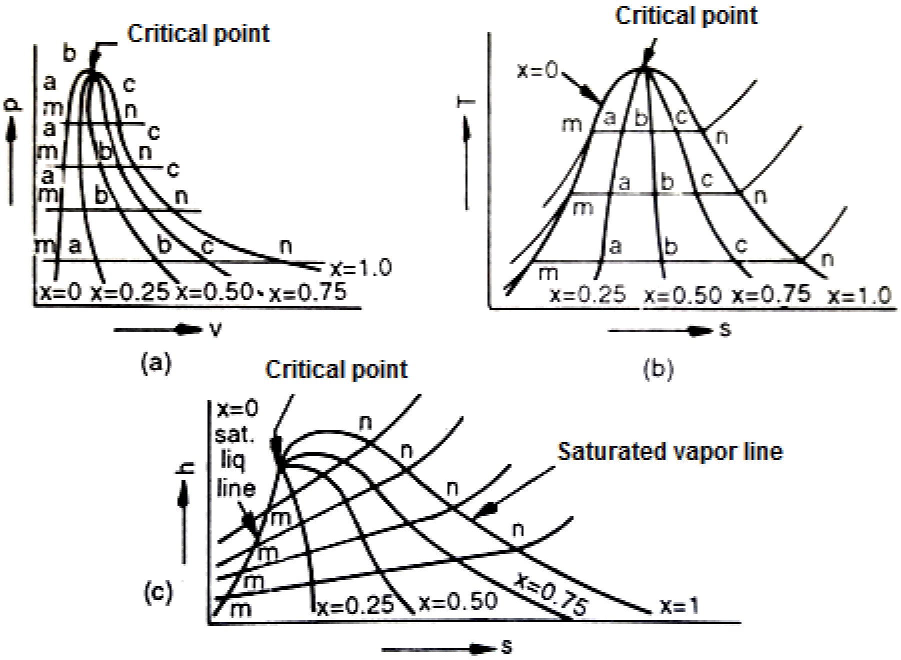


Fig. 4.10, Constant Quality lines on p-v , T-s and h-s Diagrams

- Let V be the total volume of a liquid- vapor mixture of quality x, V_f is the volume of saturated liquid, and V_g is the volume of saturated vapor, the corresponding masses be m, m_f, m_g respectively.
- Now, $m = m_f + m_g$
- $V = V_f + V_g$.

$mv = m_f v_f + m_g v_g$ where v, v_f, v_g be the specific volume of mixture, specific volume of liquid, specific volume of vapor respectively.

$$mv = m_f v_f + m_g v_g$$

$$mv = (m - m_g)v_f + m_g v_g$$

$$v = \left[1 - \frac{m_g}{m}\right]v_f + \frac{m_g}{m}v_g$$

$$v = (1-x)v_f + xv_g$$

Similarly

$$s = (1-x)s_f + xs_g$$

$$h = (1-x)h_f + xh_g$$

$$u = (1 - x)u_f + xu_g$$

Where s, h, and u refer to the mixture of quality x, suffix f and g indicate the conditions of saturated liquid and saturated vapor respectively.

$$v = (1 - x)v_f + xv_g$$

$$v = v_f + x(v_g - v_f)$$

$$v = v_f + x(v_{fg}) \qquad [v_{fg} = v_g - v_f]$$

Similarly

$$\mathrm{h} = \mathrm{h}_f + x(h_{fg})$$

$$s = s_f + x(s_{fg})$$

$$u = u_f + x(u_{fg})$$

4.8 Super heated vapor

- When the temperature of the vapor is greater than the saturation temperature corresponding to given pressure, the vapor is said to be super heated. (state 1 in fig.4.11)
- The difference between the temperature of the super heated vapor and the saturation temperature at that pressure is called the ***super heat*** or ***degree of super heat.***
- Degree of super heat = $T_{\sup} - T_{sat}$

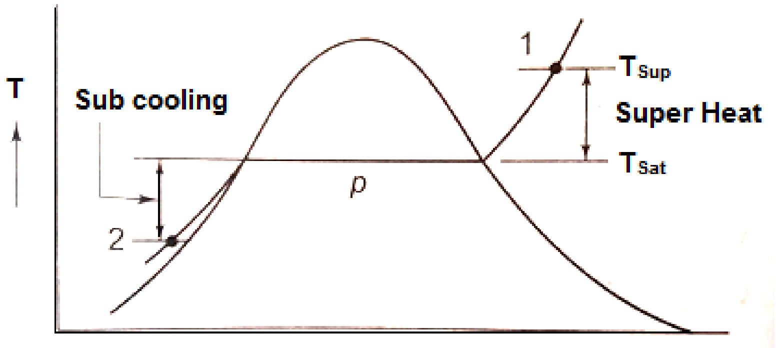


Fig. 4.11, Super Heat and Sub cooling

Sub cooling

- When the temperature of the liquid is less than the saturation temperature at the given pressure, the liquid is called Sub cooled liquid or Compressed liquid.

OR

When the liquid is cooled below its saturation temperature at a certain pressure it is said to be sub cooled.

Degree of sub cooling = $T_{sat}-T_2$ [From fig 4.11]

4.9 Measurement of steam quality

Introduction

- The state of a pure substance gets fixed if two independent properties are given. A pure substance is thus said to have two degrees of freedom. Of all thermodynamic properties, it is easiest to measure the pressure and temperature of the substance.
- Therefore, when pressure and temperature are independent properties, we can measure them to determine the state of a substance. This is done in the compressed liquid region or super heated region.
- If the substance is in the saturated state or two-phase region, the measured values of pressure and temperature could apply equally well saturated liquid point f, saturated vapor point g, or the mixtures of any quality. Of the two properties p and t only one is independent, other is dependent property.
- In order to fix up the state of the mixture, apart from either pressure or temperature, one more property such as specific volume, enthalpy or composition of the mixture (quality) is required to be known.
- Since it is relatively difficult to measure specific volume of a mixture, devices such as calorimeters are used for measurement of quality or enthalpy of mixture.

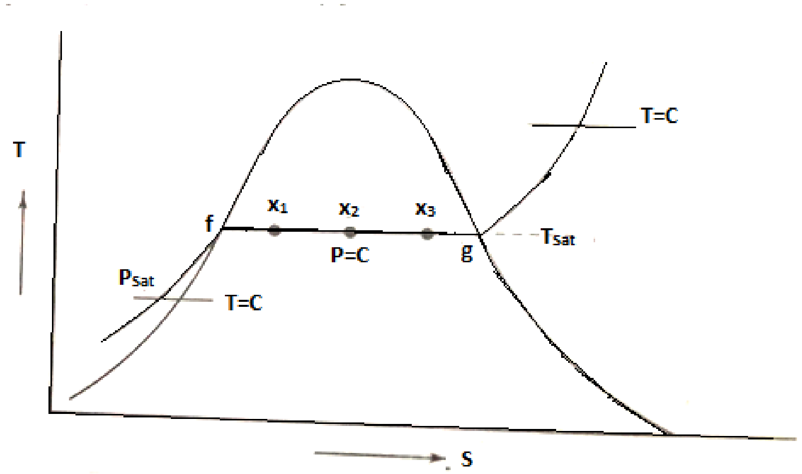


Fig.4.12 Quality of liquid -vapor Mixture

- In the measurement of quality, the object is always to bring the state of the substance from two-phase region to a single phase or superheated region, where both pressure and temperature are independent, and measured to fix the state, either by adiabatic throttling or electric heating.

4.9.1 Throttling Calorimeter

- In the throttling calorimeter, a sample of wet steam of mass m and at pressure p_1 is taken from the steam through a perforated sampling tube as shown in fig. 4.14. Then it is throttled by a partially opened valve to a pressure p_2, measured by mercury manometer, and temperature T_2, so that after throttling the steam is in the super heated region. The process is shown on T-S and h-s diagrams in Fig. 4.13. The steady flow energy equation gives the enthalpy after throttling as equal to enthalpy before throttling.

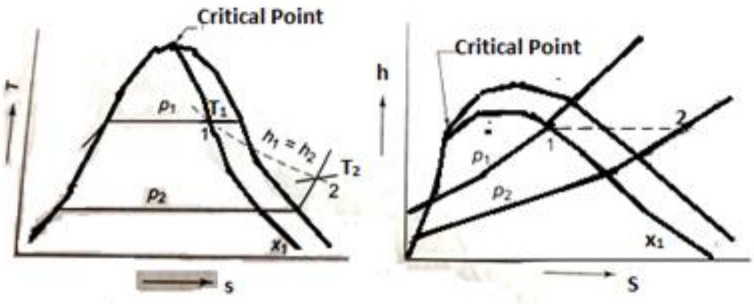


Fig.4.13 T-s and h-s diagrams

$$h_1 = h_2$$

$$h_{f1} + x_1 h_{fg1} = h_2$$

$$x_1 = \left[\frac{h_2 - h_{f1}}{h_{fg1}}\right]$$

- With p_2, and T_2 being known h_2 can be found out from the super heated steam table. The values of h_{f1} and h_{fg1} are taken from the saturated steam table corresponding to pressure p_1.

- To be sure that steam after throttling is in the single-phase or super heated region, a minimum of 5^0C super heat is desired.

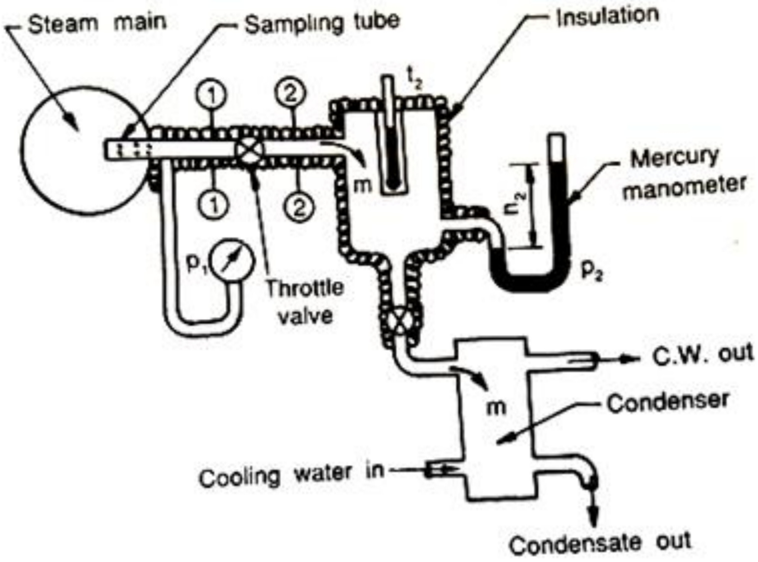


Fig.4.14 Throttling calorimeter

4.9.2 Combined Separating and throttling calorimeter

- When the steam is very wet and the pressure after throttling is not low enough to take the steam to the super heated region, then a combined separating and throttling calorimeter is used for measuring the quality. Steam from the main is first passed through a separator (fig. 4.15), where some part of the moisture separates out due to the sudden change in direction and falls by gravity, and the partially dry vapor is then throttled and taken to the super heated region. In the fig. 4.15 process 1-2 represents the moisture separation from the wet sample of steam at constant pressure p_1, and process 2-3 represents throttling to pressure p_2.

$$h_3 = h_2 = h_{f1} + x_2 h_{fg1}.$$

- Therefore, the quality of steam after partial moisture separation can be evaluated.
- If m kg of steam is taken through the sampling tube in t seconds. m_1 kg of it is separated, and m_2 kg is throttled and then condensed to water and collected, then $m=m_1+m_2$.and at state 2, the mass of dry vapor will be $x_2 m_2$. Therefore the quality of the sample of the steam at state 1, x_1 is given by

$$\frac{\text{Mass of dry vapor at state 1}}{\text{Mass of (liquid-vapor) mixture at state 1}}$$

$$= \frac{x_2 m_2}{m_1 + m_2}$$

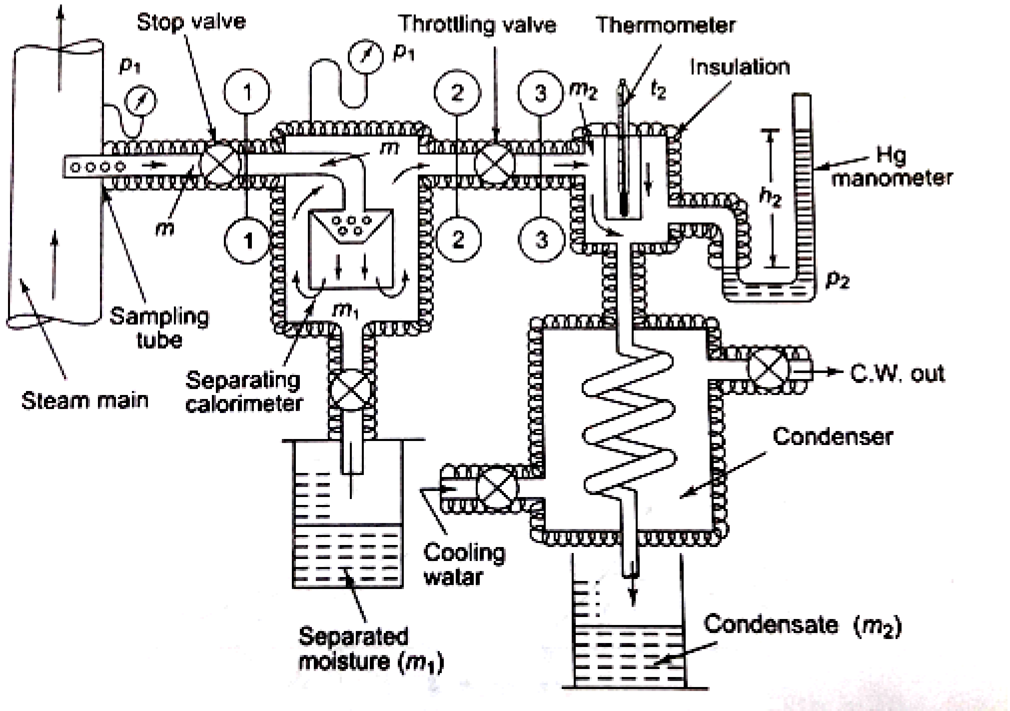
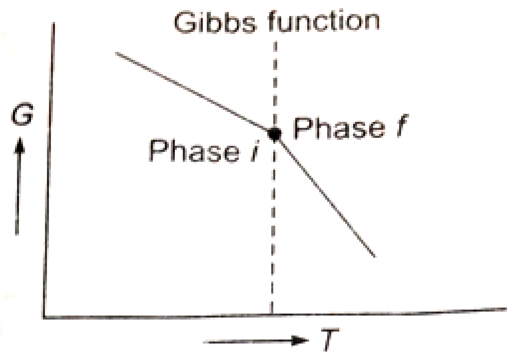


Fig. 4.15 Seperating and Throttling Calorimeter

4.10 Clausius Clayperon Equation

- During Phase transitions like melting, vaporization and sublimation, the temperature and pressure remains constant, while the entropy and volume change. If *x* is the fraction of initial phase I which has been transformed to final phase *f*, then



$$s = (1-x)s^{(i)} + xs^{(f)}$$

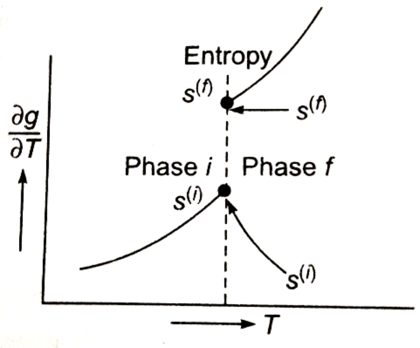
$$v = (1-x)v^{(i)} + xv^{(f)}$$

Where s and v are linear functions of x.

- For first order phase transition, the heat transferred per mole(or per kg) is the latent heat given by

$$l = T\left\{s^{(f)} - s^{(\mathrm{i})}\right\}$$

Which indicates the change in entropy.

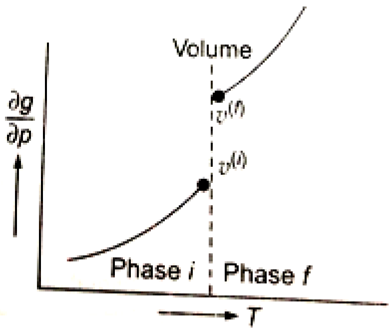


$$dg = -sdT + vdp$$

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

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

- A phase change of the first order is known as any phase change that satisfies the following requirements.



1. There are changes of entropy and volume.
2. The first-order derivatives of Gibbs function changes discontinuously.

- Let us consider the first-order phase transition of one mole of substance from phase *i* to phase *f*.

  Using the first Tds equation

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

- For the phase transition which is reversible isothermal and isobaric and integrating over the whole change of phase, and since $\left(\frac{\partial P}{\partial T}\right)_v$ is independent of *v*

$$T\left\{s^{(f)} - s^{(\mathrm{i})}\right\} = T\left(\frac{\partial P}{\partial T}\right)\left\{v^{(f)} - v^{(\mathrm{i})}\right\}$$

$$\therefore \frac{\partial P}{\partial T} = \frac{\left\{s^{(f)} - s^{(\mathrm{i})}\right\}}{\left\{v^{(f)} - v^{(\mathrm{i})}\right\}} = \frac{l}{T\left\{v^{(f)} - v^{(\mathrm{i})}\right\}}$$

The above equation is known as ***clausius-clapeyron*** equation

The ***clausius-clapeyron*** equation can also be determined in another way. For a reversible process at constant pressure, temperature, the Gibbs function remains constant.

Therefore, for the first –order phase change at T and p

$$g^{(i)} = g^{(f)}$$

And for a phase change at T+dT, and P+dP

$$g^{(i)} + dg^{(i)} = g^{(f)} + dg^{(\mathrm{f})}$$

Subtracting

$$dg^{(i)} = dg^{(\mathrm{f})}$$

$$-s^{(i)}dT + v^{(i)}dp$$

$$-s^{(\mathrm{f})}dT + v^{(\mathrm{f})}dp$$

$$\therefore \frac{\partial P}{\partial T} = \frac{\left\{s^{(f)} - s^{(\mathrm{i})}\right\}}{\left\{v^{(f)} - v^{(\mathrm{i})}\right\}} = \frac{l}{T\left\{v^{(f)} - v^{(\mathrm{i})}\right\}}$$

ENGINEERING THERMODYNAMICS

Unit V

Objectives:

- To introduce the students to Ideal gas and real gas behavior, gravimetric and volumetric behavior of mixture of gases.

Syllabus:

Perfect Gas Laws – Equation of State, specific and Universal Gas constants –various Non-flow processes, Heat and Work Transfer, changes in Internal Energy Enthalpy and Entropy , Throttling and Free Expansion Processes, Joule-Thompson coefficient – work Transfer during Flow processes – Deviations from perfect Gas Model – Vander Waals Equation of State, Law of Corresponding States, Compressibility charts.

Mixtures of perfect Gases – Mole Fraction, Mass fraction Gravimetric and volumetric Analysis – Dalton's Law of partial pressure, Avogadro's Laws of additive volumes, Equivalent Gas constant and Molar Internal Energy, Enthalpy, specific heats and Entropy of mixture of perfect Gases.,

Outcomes:

Students will be able to

- Distinguish between Ideal, real gas behaviors and work and heat Interactions in various Non-flow processes.
- Define universal and characteristic gas constants.
- Define Dalton's Law, Avogadro's Law of additive volumes, Equivalent gas constant.
- Calculate the changes in Internal energy, enthalpy and entropy of Ideal gases and gas mixtures.
- Evaluate mole fraction, mass fraction, molar Internal energy, enthalpy and specific heats of mixtures.

5.1. Equation of state of a Gas

- The functional relationship among the properties, pressure P, molar specific volume v, and temperature T is known as equation of state, which may be expressed in the form ,

$$f\,(P,\ v,T)=0.$$

- If two of these properties of a gas are known, the third can be evaluated from the equation of state.
- In thermodynamics we distinguish between

a) Perfect gases

b) Ideal gases

c) Real gases

(a) Perfect Gas

The equation $\frac{pv}{T}=const$ was derived assuming that Molecules of a gas are point masses.

There are no attractive nor repulsive forces between the molecules.

Perfect gas is one which obeys the above equation.

- Various forms of writing perfect gas equation of state.

(i) $p\bar{v}=\bar{R}T$ where P is absolute pressure

$\bar{v}$ is molar specific volume.

$\bar{R}$ is universal gas constant.

T is absolute temperature.

$\bar{R}=\text{m}.R$ where m is molecular weight. and R is characteristic gas constant.

$$\bar{R}=Molecular-weight\left(m\right)\times R$$

$$R=\frac{\bar{R}}{Molecular-weight\left(m\right)}$$

Substitute this value in the above equation, we get

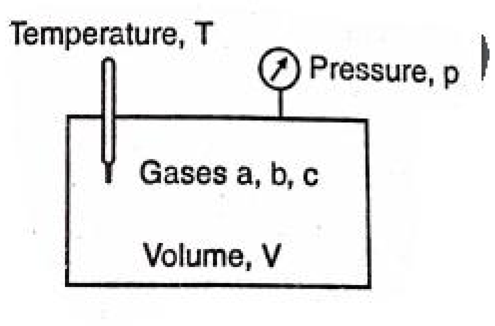
$$\text{(ii)} \qquad p\bar{v}=mRT\,.$$

(iii) But $n = \frac{m}{\text{«}}$ where m is the mass of the gas and n is number of moles.

Substituting this value we get

$$\text{(iv)} \qquad p\bar{v} = \frac{m}{n}.RT \ .$$

$$p(n\bar{v}) = mRT$$



(v) $pV = mRT$ Where V is the total volume and

(vi) $pV = n\bar{R}T$ is also obtained.

(vii) $pv = RT$ Where v is specific volume and R is characteristic gas constant.

$\bar{R}$ is universal gas constant. Its value is 8.314kJ/kmol.K.

R is characteristic gas constant. $= \frac{\bar{R}}{m}$

$$R_{air} = \frac{8.3143}{28.96} = 0.287 \frac{kJ}{kgK} \ .$$

$$R_{o_2} = \frac{8.3143}{32} = 0.262 \frac{kJ}{kgK} \ .$$

- A perfect gas has <u>constant specific heats</u>.
- An <u>Ideal gas</u> is one which obeys the above equation, but whose specific heats are functions of temperature alone.

(b) Ideal Gas:

- **A** hypothetical gas which obeys the law $pv = \frac{m}{n}RT$ or $p\bar{v} = \bar{R}T$ at all pressures and temperatures is called an Ideal Gas.

Real gases do not confirm to this equation of state with complete accuracy. As $p \to 0$ or $T \to \infty$ the real gas approaches Ideal behavior.

(c) Real Gases

- Real gases deviate from ideal behavior because real gases have intermolecular forces and real gases have volume.
- If there were no intermolecular forces, gases could not be made into liquids and solids because they would not stick together.
- Conditions of low temperature, low volume, high number of moles, and high pressure puts molecules close together, which makes the factors of intermolecular forces and gas volume to become important.

AVAGADRO'S LAW

It states that the volume of a g.mol of all gases at the pressure of 760mm Hg and temperature of 0^0 C is the same and is equal to 22.4lits.**(STP)**

1gmol of a gas has a volume of 22.4 x 10^3cm^3 and 1 kg mol of gas has a volume of 22.4m^3 at Normal temperature and pressure.**(NTP)**

5.2 Enthalpy and Internal energy of an Ideal gas:

Enthalpy and Internal energy for Ideal gas are functions of temperature alone.

$$dh = Tds + vdp$$

From Second Tds Equation, $Tds = c_p dt - T\left(\frac{\partial V}{\partial T}\right)_p dp$

$$dh = c_p dt - T\left(\frac{\partial V}{\partial T}\right)_p dp + vdp \to \quad dh = c_p dt + \left(v - T\left(\frac{\partial V}{\partial T}\right)_p\right)dp \text{ ---------- (1)}$$

Let h=h(T,p)

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dt + \left(\frac{\partial h}{\partial p}\right)_T dp \text{ ------------------------- (2)}$$

Compare the coefficients of eq. (1) and (2)

We get $\left(\frac{\partial h}{\partial p}\right)_T = \left(v - T\left(\frac{\partial V}{\partial T}\right)_p\right)$ For Ideal Gas $pv = RT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{P} = \frac{v}{T} \qquad \therefore \left(v - T\left(\frac{\partial V}{\partial T}\right)_p\right) = 0 \qquad \therefore \left(\frac{\partial h}{\partial p}\right)_T = 0$$

So $dh = c_p dT$.

It proves that, for Ideal gas enthalpy is not changing with pressure. Similarly we can prove enthalpy is not changing with volume either.

So Enthalpy of an Ideal gas is a function of temperature only.

- Internal Energy of an Ideal gas is also function of temperature alone.

$$du = Tds - pdv$$

From 1st Tds Equation $Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$

$$du = c_v dT + \left(T\left(\frac{\partial p}{\partial T}\right)_v - p\right)dv$$

Let u = u(T,v)

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

Comparing the coefficients

$$\left(\frac{\partial u}{\partial v}\right)_t dv = \left(T\left(\frac{\partial p}{\partial T}\right)_v - p\right)dv$$

From Ideal gas Equation, $pv = RT$

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

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = 0$$

$\left(\frac{\partial u}{\partial v}\right)_t$ =0, similarly we can show that internal energy is not a function of Pressure either.

$\therefore du = c_v dT$. Therefore Internal energy is a function of Temperature alone.

u = u (T) only. Now

Enthalpy H= sum of internal energy U + Flow energy (PV)

Specific enthalpy = $h = \left(\frac{H}{m}\right) \rightarrow h = u + pv$

For an Ideal gas $pv = RT$

$dh = du + RdT$ $\qquad\qquad du = c_v dT$ for Ideal gas.

$$dh = \left[c_v + R\right] dT$$

Since h is also a function of temperature alone for ideal gas

$$c_p = \left[\frac{dh}{dt}\right]_p \rightarrow dh = c_p dT$$

From the above Two equations

$$c_v + R = c_p$$

$$c_p - c_v = R$$

- The ratio of $\frac{c_p}{c_v}$ is of importance in Ideal gas computations
- It is designated by the symbol **γ**(gama)

$$\therefore \frac{c_p}{c_v} = \yen \rightarrow \qquad c_p = \yen c_v \rightarrow \qquad (\yen - 1)c_v = R$$

$$c_v = \frac{R}{(\yen - 1)} \qquad\qquad c_p = \frac{\yen R}{(\yen - 1)}$$

- **Variation of specific heat with temperature**

  The specific heat of a real gas varies with temperature. The functional relationships denoting this variation are determined from experimental tests. Table 4.1 lists several formulas hat predict the specific heat of a gas at a given temperature. Figure 4.2 shows a diagram of the specific heat variation with temperature for a few gases.

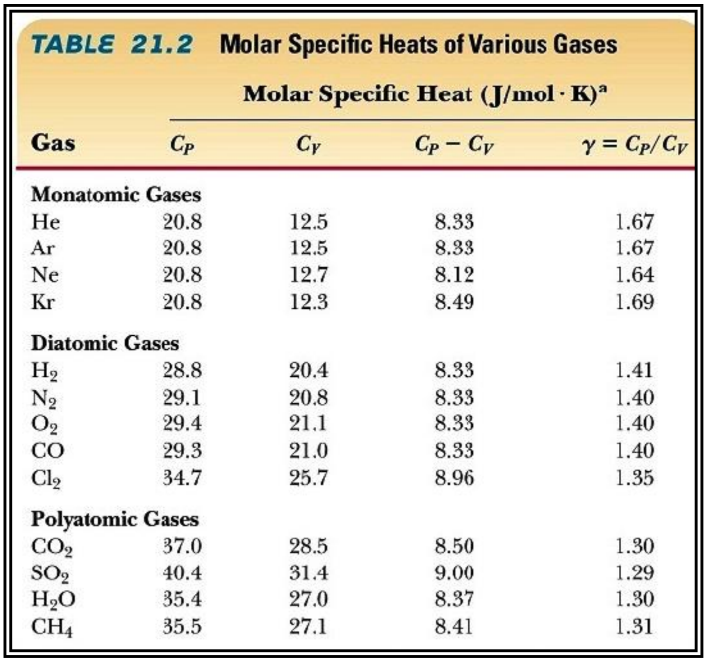
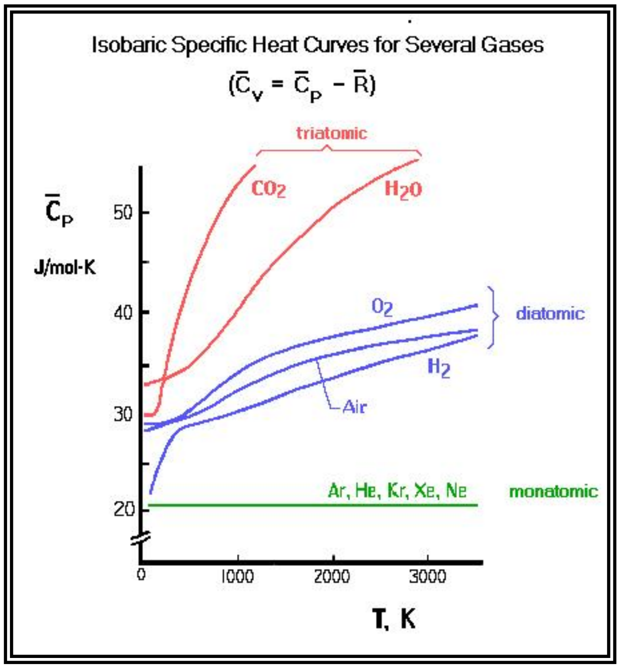


TABLE 21.2 Molar Specific Heats of Various Gases

Gas	Molar Specific Heat (J/mol · K)^a			
	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31



Entropy change of an Ideal Gas

- From the general property relations

$$Tds = du + pdv$$

$$Tds = dh - vdp$$

$$ds = \frac{du}{T} + \frac{pdv}{T}$$

$$ds = \frac{c_v dT}{T} + \frac{R}{v}dv \quad (\therefore du = c_v dT)$$

$$\int_1^2 ds = \int_1^2 \frac{c_v dT}{T} + \int_1^2 \frac{R}{v}dv \rightarrow \quad \boxed{s_2 - s_1 = c_v\left[\ln\frac{T_2}{T_1}\right] + R\left[\ln\frac{v_2}{v_1}\right]}$$

Also

$$ds = \frac{dh}{T} - \frac{vdp}{T} \qquad \therefore dh = c_p dT$$

$$ds = \frac{c_p dT}{T} - \frac{R}{p}dp$$

$$\int_1^2 ds = \int_1^2 \frac{c_p dT}{T} - \int_1^2 \frac{R}{p}dp \Rightarrow \quad \boxed{s_2 - s_1 = c_p\left[\ln\frac{T_2}{T_1}\right] - R\left[\ln\frac{p_2}{p_1}\right]}$$

Since $R = c_p - c_v \rightarrow$ $\boxed{s_2 - s_1 = c_p\left[\ln\frac{v_2}{v_1}\right] + c_v\left[\ln\frac{p_2}{p_1}\right]}$

Reversible Adiabatic Process

- The general property relation for an ideal gas may be written as

$$Tds = du + pdv = c_v dT + pdv$$

$$Tds = dh - vdp = c_p dT - vdp$$

For a reversible adiabatic change, ds=0

$$c_v dT = -pdv$$

$$c_p dT = vdp$$

And by division

$$\frac{c_p}{c_v} = \gamma = -\frac{vdp}{pdv}$$

$$\frac{dp}{p} + \gamma\frac{dv}{v} = 0$$

Or

$$\ln p + \gamma \ln v = \ln c \quad =\!\!\Rightarrow \quad \boxed{pv^{\gamma} = C}$$

For an Ideal gas

$$pv = RT$$

From the equation, $pv^{\gamma} = C$

$$p = C.v^{-\gamma}$$

$$p = \frac{RT}{v} = C.v^{-\gamma} =\!\!\Rightarrow RT = Cv^{1-\gamma}$$

$$\boxed{Tv^{\gamma-1} = C}$$

Between states 1 and 2

$$\boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}}$$

Similarly

$$v = \left(\frac{c}{p}\right)^{\frac{1}{\gamma}}$$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}}$$

$$T\left(p^{\frac{1-¥}{¥}}\right)=C\rightarrow$$

The Internal energy change of an Ideal gas for a reversible adiabatic process is given by

$$Tds = du + pdv$$

$$\int_1^2 du = -\int_1^2 pdv = -\int_1^2 \frac{c}{v^{¥}}\,dv \rightarrow$$

$$\boxed{u_2 - u_1 = \frac{RT_1}{¥ - 1}\left[\left(\frac{p_2}{p_1}\right)^{\frac{¥-1}{¥}} - 1\right]}$$

The change in enthalpy of an ideal g

$$Tds = dh - vdp$$

$$\int_1^2 dh = \int_1^2 vdp = \int_1^2 \left(\frac{c}{p}\right)^{\frac{1}{¥}} dv \rightarrow$$

$$\boxed{h_2 - h_1 = \frac{¥ RT_1}{¥ - 1}\left[\left(\frac{p_2}{p_1}\right)^{\frac{¥-1}{¥}} - 1\right]}$$

The work done by an ideal gas in a reversible adiabatic process is given by

$$¢\, w = -du$$

i.e. the work is done at the expense of Internal energy.

$$\therefore W = m(u_2 - u_1) = \frac{mRT_1}{¥ - 1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{¥-1}{¥}}\right]$$

In a Steady flow Process where both flow and external work are involved, we have from S.F.E.E

$$\mathrm{W} = \frac{¥}{¥ - 1} p_1 v_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{¥-1}{¥}}\right]$$

Reversible Isothermal Process

When an ideal gas of mass m undergoes a reversible Isothermal process from state 1 to state 2, the work done is given by

$$\int_1^2 ¢W = \int_1^2 pdv = \int_1^2 \frac{mRT}{V}dV = mRT\ln\frac{V_2}{V_1} = mRT\ln\frac{p_1}{p_2}$$

Polytropic Process

An equation of the form $pv^n = C$, where n is a constant can be used approximately to describe many processes which occur in practice. Such a process is called a polytropic process. It is not adiabatic but it can be reversible.

It may be noted that γ is a property of a gas but n is not. The value of n depends on the process.

From the two states of the process,

$$p_1 v_1^{\,n} = p_2 v_2^{\,n}$$

$$n = \frac{\log p_1 - \log p_2}{\log v_2 - \log v_1}$$

Two other relations of a polytropic process are

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} \text{ and } \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1}$$

The entropy change in a polytropic process is given by 3 equations.

$$\boxed{s_2 - s_1 = \frac{n - ¥}{(¥ - 1)(n-1)} R\ln\left[\frac{T_2}{T_1}\right]}$$

$$\boxed{s_2 - s_1 = \frac{n - ¥}{(¥ - 1)n} R\ln\left[\frac{P_2}{P_1}\right]}$$

$$\boxed{s_2 - s_1 = -\frac{n - ¥}{(¥ - 1)} R\ln\left[\frac{v_2}{v_1}\right]}$$

Heat and work in a polytropic process

Using the first law to unit mass of an ideal gas

$$Q - W = u_2 - u_1 = c_v\left(T_2 - T_1\right) = \frac{R}{¥ - 1}\left(T_2 - T_1\right)$$

$$= \frac{p_2 v_2 - p_1 v_1}{\gamma - 1}$$

For a steady flow of unit mass of an Ideal gas

$$Q - W = \gamma \left[\frac{p_2 v_2 - p_1 v_1}{\gamma - 1} \right]$$

Integral Property Relations in a Polytropic process

In a $pv^n = c$, process

$$\int_1^2 pdv = \int_1^2 \frac{p_1 v_1{}^n}{v^n} dv = \frac{p_1 v_1}{n-1}\left[1 - \left(\frac{v_1}{v_2}\right)^{n-1}\right] = \frac{p_1 v_1}{n - 1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right]$$

Similarly for $-\int_1^2 vdp$

$$= \frac{np_1 v_1}{n-1}\left[1 - \left(\frac{v_1}{v_2}\right)^{n-1}\right]$$

The integral of Tds is obtained from property relation

$$Tds = du + pdv$$

$$\int_1^2 Tds = \int_1^2 du + \int_1^2 pdv$$

$$= u_2 - u_1 + \int_1^2 pdv$$

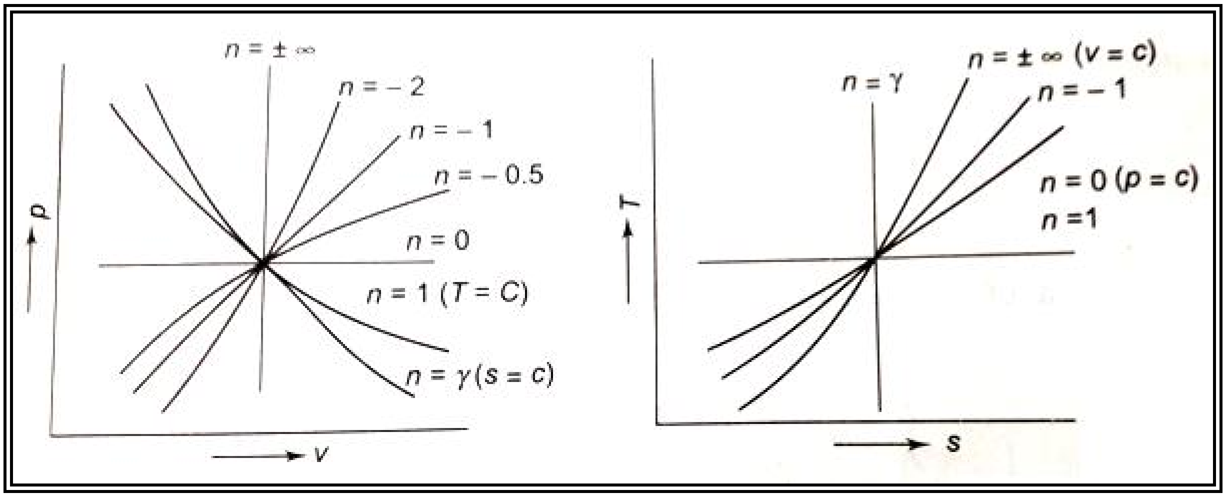
$$\int_1^2 Tds = \frac{\gamma - n}{(\gamma - 1)(n-1)} R\left(T_1 - T_2\right)$$

$$\int_1^2 Tds = c_v \frac{\gamma - n}{1-n} \Delta T$$

$\int_1^2 Tds = c_n \Delta T$ where c_n is called polytropic specific heat.

For $n > \gamma$ there will be positive heat transfer and gain in entropy. For $n < \gamma$, heat transfer will be negative and entropy of the gas would decrease.

The polytropic process for various values of n is shown in fig.



Deviation from ideal gas behaviour:

- A gas which obeys the gas laws and the gas equation PV = nRT strictly at all temperatures and pressures is said to be an ideal gas.
- The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another. But no real gas strictly obeys the gas equation at all temperatures and pressures.
- Deviations from ideal behaviour are observed particularly at high pressures or low temperatures.

The deviation from ideal behaviour is expressed by introducing a factor Z known as compressibility factor in the ideal gas equation.

Z may be expressed as $Z = PV / nRT$

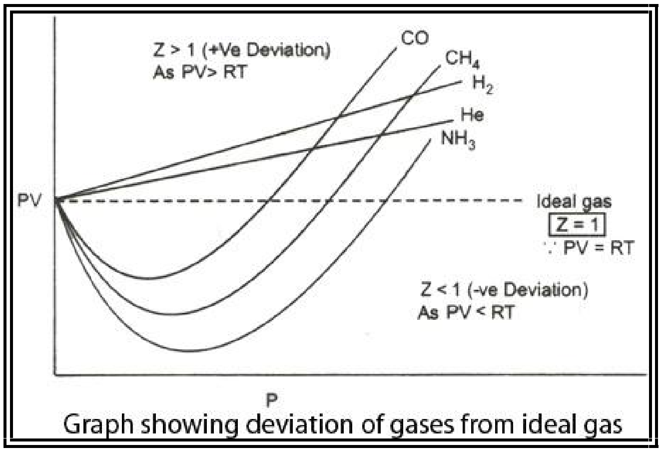
- In case of ideal gas, $PV = nRT \therefore Z = 1$

1. In case of real gas, $PV \neq nRt \therefore Z \neq 1$

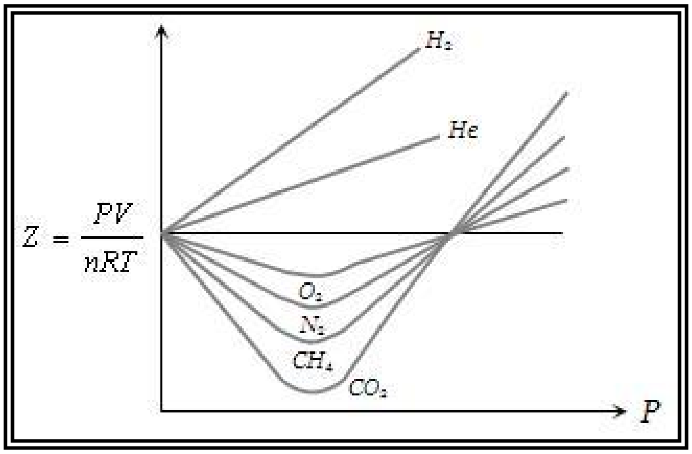
Thus in case of real gases Z can be < 1 or > 1

- When $Z < 1$, it is a negative deviation.
  - It shows that the gas is more compressible than expected from ideal behaviour.

1. When $Z > 1$, it is a positive deviation.
   - It shows that the gas is less compressible than expected from ideal behaviour.



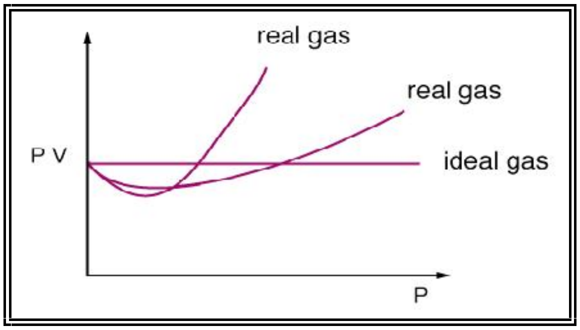
Graph showing deviation of gases from ideal gas



Causes of deviation from ideal behavior

The causes of deviations from ideal behavior may be due to the following two assumptions of kinetic theory of gases.

- The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.
- The forces of attraction between gas molecules are negligible.
- The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas.
- But at low temperature or at high pressure, the molecules being in compressible the volumes of molecules are no more negligible as compared to the total volume of the gas.



The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored.

Vander Waals' Equation of State for a Real Gas

The deviations from ideal gas behaviour can be ascertained to the following faulty assumptions by kinetic theory of gases.

- The real volume of the gas molecules is negligible when compared to the volume of the Container.

- There are no forces of attraction or repulsion between the gas molecules.

Hence van der Waal suggested the following corrections:

- The gas molecules possess finite volume and hence should not be neglected. It is especially true at high pressures and low temperatures and should be accounted for.
- In case of real gases, both the forces of attraction as well as repulsion operate between gas molecules.

Note: If the gases obey the kinetic theory of gases, then they cannot be compressed since the attractions between the gas molecules are negligible.

Also the following corrections are applied by vander Waals to the ideal gas equation:

Volume correction:

The volume available for the gas molecules is less than the volume of the container, V.

The available volume is obtained by subtracting excluded volume of 'n' moles of gas, nb from the volume of the container.

Available volume = V - nb

where n = Number of moles of real gas

V = Volume of the gas

b = A constant whose value depends upon the nature of the gas

The ideal gas equation can be written after correcting for this as:

$P(V-nb) = nRT$

Pressure correction:

- Take a real gas of pressure P
- The molecular attraction between one molecule to another molecule the pressure generated ,at that time is the pressure force considered as negligible(not considered)
- The pressure force generated in this container more in case of Ideal gas than the Real gas
- Suppose the pressure generated by molecular attraction in the real its molecules in the reverse direction
- The pressure force in case of Ideal Gas =(P+p) (p is the pressure lost by the gas molecules due to attractions).

p = This small pressure p would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore $p \propto n/v$ (concentration of molecules which are hitting the container's wall)
$P \propto n/v$ (concentration of molecules which are attracting these molecules) $\Rightarrow$ $p \propto n^2/v^2$
$P = an^2/v^2$ where a is the constant of proportionality which depends on the nature of gas.
A higher value of 'a' reflects the increased attraction between gas molecules.

Hence ideal pressure

$P_i = (P + an^2 / V^2)$

Here,

n = Number of moles of real gas

V = Volume of the gas

a = A constant whose value depends upon the nature of the gas

Substituting the values of ideal volume and ideal pressure in ideal gas equation i.e. pV=nRT, the modified equation is obtained as

$(P + an^2 / V^2) (V-nb) = nRT$

$(P + a(n / V)^2) (V-nb) = nRT$

$(P + a(n / V)^2) \rightarrow$ Ideal pressure
$(V-nb) \rightarrow$ Ideal volume
P = measured pressure
$a(n / V)^2$ = correction factor to account for intermolecular attractions
V = measured volume
nb = correction factor to account for the finite size of the molecules
a=Vander Waals attraction constant
b=volume for a given gas.
Some salient feature of a & b are:

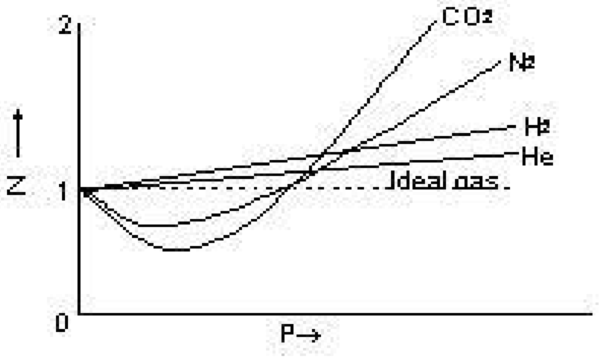
- For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of volume (b).
- The gas having higher value of 'a' can be liquefied easily and therefore H_2 & He are not liquefied easily.
- The units of a = litre^2 atm mole^{-2} & that of b = litre mole $^{-1}$
- The numerical values of a & b are in the order of 10^{-1} to 10^{-2} & 10^{-2} to 10^{-4} respectively.

Higher is the value of 'a' for a given gas, easier is the liquefaction.

Different forms of Van der Waal's equation

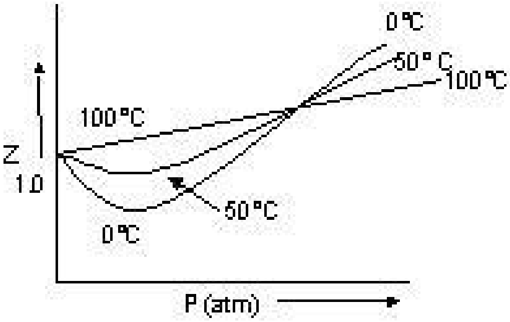
- **At low pressures:**

'V' is large and 'b' is negligible in comparison with V.
The Vander Waals equation reduces to:
$(P + a / V^2) V = RT;$
$PV + a/ V = RT$
$PV = RT – a/V$ or $PV < RT$
This accounts for the dip in PV vs P isotherm at low pressures.



- **For high pressures**

a/V^2 may be neglected in comparison with P.
The Vander Waals equation becomes
$P (V – b) = RT$
$PV – Pb = RT$
$PV = RT + Pb$ or $PV > RT$
This accounts for the rising parts of the PV vs P isotherm at high pressures.



- **At very low pressures:**

V becomes so large that both b and a/V^2 become negligible and the Vander Waals equation reduces to $PV = RT$. This shows why gases approach ideal behaviour at very low pressures.

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:
  - Specifying the number of moles of each component, called **molar analysis,**
  - Specifying the mass of each component, called **gravimetric analysis.**

Consider a gas mixture composed of k components.

The mass of the mixture mm is the sum of the masses of the individual components, and the mole number of the mixture N_m is the sum of the mole numbers of the individual components

$$m_m = \sum_{i=1}^{k} m_i \quad \text{and} \quad N_m = \sum_{i=1}^{k} N_i$$

- The ratio of the mass of a component to the mass of the mixture is called the **mass fraction**

  It is donated by **m_f** $$mf_i = \frac{m_i}{m_m}$$

- The ratio of the mole number of a component to the mole number of the mixture is called the **Mole fraction**

  It is denoted by y: $$y_i = \frac{N_i}{N_m}$$

Note that

$$\sum_{i=1}^{k} mf_i = 1 \quad \text{and} \quad \sum_{i=1}^{k} y_i = 1$$

The mass of a substance can be expressed in terms of the mole number N and molar mass M of the substance as m =NM. Then the **apparent** (or **average**) **molar mass** and the **gas constant** of a mixture can be expressed as

$$M_m = \frac{m_m}{N_m} = \sum_{i=1}^{k} \frac{N_i}{N_m} M_i = \sum_{i=1}^{k} y_i M_i \qquad (kg / kmol)$$

The apparent (or average) gas constant of a mixture is expressed as

$$R_m = \frac{R_u}{M_m} \qquad (kJ / kg \cdot K)$$

R_m is given as

$$R_m = \sum_{i=1}^{k} mf_i R_i$$

To change from a mole fraction analysis to a mass fraction analysis,

$$mf_i = \frac{y_i M_i}{\sum_{i=1}^{k} y_i M_i}$$

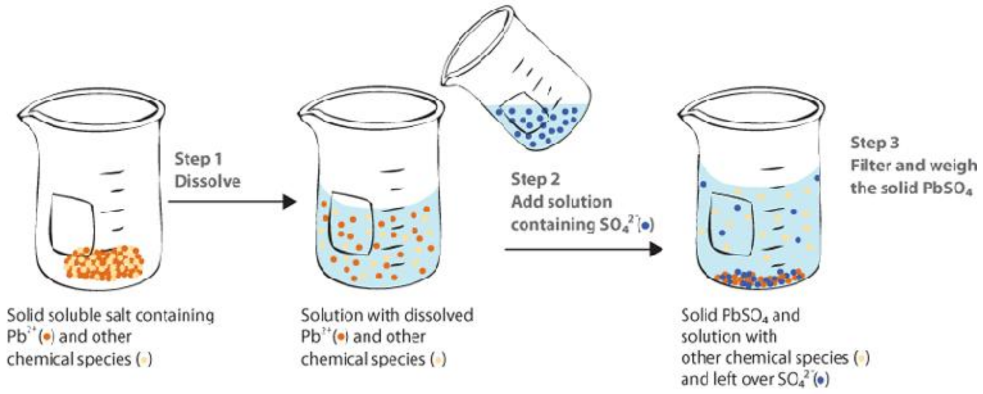
To change from a mass fraction analysis to a mole fraction analysis,

$$y_i = \frac{mf_i / M_i}{\sum_{i=1}^{k} mf_i / M_i}$$

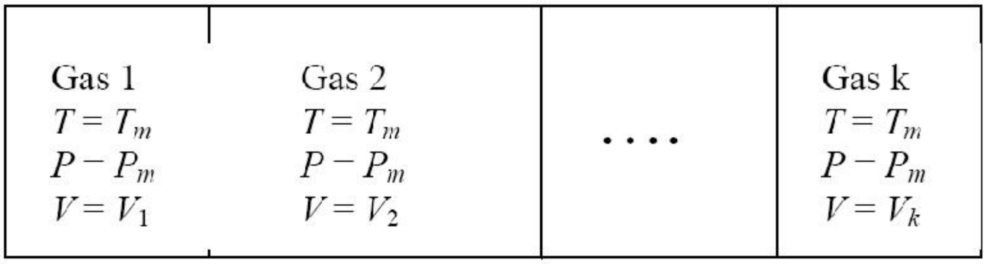
Gravimetric analysis

- Gravimetric analysis is a technique through which the amount of an analyte (the ion being analyzed) can be determined through the measurement of mass.
- Gravimetric analyses depend on comparing the masses of two compounds containing the analyte. The principle behind gravimetric analysis is that the mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound. In order for the analysis to be accurate, certain conditions must be met:

1. The ion being analyzed must be completely precipitated.
2. The precipitate must be a pure compound.
3. The precipitate must be easily filtered.



Volume fraction :
Divide the container into k sub containers, such that each sub container has only one of the gases in the mixture at the original mixture temperature and pressure.



Gas 1 $T = T_m$ $P - P_m$ $V = V_1$	Gas 2 $T = T_m$ $P - P_m$ $V = V_2$	. . . .	Gas k $T = T_m$ $P - P_m$ $V = V_k$

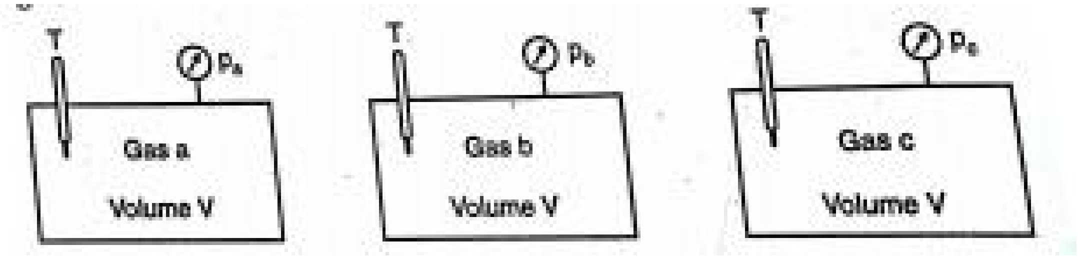
- The prediction of the P-v-T behaviour of gas mixtures is usually based on two models: Dalton's law of additive pressures and Amagat's law of additive volumes. Both models are described and discussed below.

Amagat's law of additive volumes states that the volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.

Amagat's law:

$$V_m = \sum_{i=1}^{k} V_i (T_m , P_m)$$

Where, $v_i = v_1 + v_2 + v_3$ +----------v_i, Volume of number of constituent gases. v_m = volume of mixture; T_m = temperature of mixture & P_m = Pressure of mixture



The volume fraction of the vf_i of any component is

$$vf_i = \frac{V_i (T_m , P_m)}{V_m}$$

and

$$\sum_{i=1}^{k} vf_i = 1$$

For an ideal gas mixture

$$V_i = \frac{N_i R_u T_m}{P_m} \quad and \quad V_m = \frac{N_m R_u T_m}{P_m}$$

Taking the ratio of these two equations gives

$$vf_i = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

The volume fraction and the mole fraction of a component in an ideal gas mixture are the same.

Dalton's Law of partial pressure:

- In a mixture of gases, which don't react with each other, total pressure of the mixture is equal to the sum of the partial pressures of the constituent/individual gases, at the same temperature & volume as that of the mixture.

or

Partial pressure of an individual gas: It is the pressure exerted by an individual gas when it alone occupies the mixture volume at the mixture temperature

i.e, $p = p_1 + p_2 \ldots\ldots p_n$ (because, partial pressure = mole fraction x total pressure p)Partial pressure :

- The partial pressure of component i is defined as the product of the mole fraction and the mixture pressure according to Dalton's law. For the component i

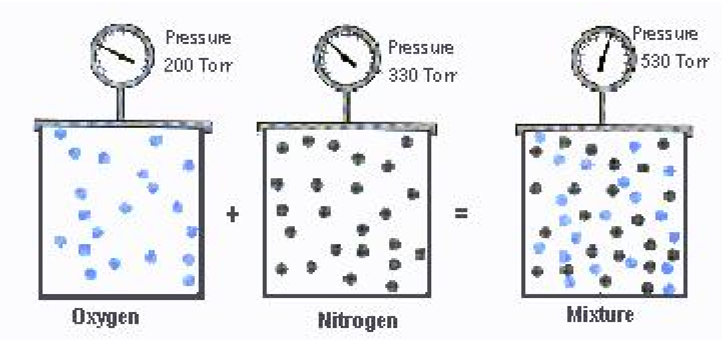
$$P_i = y_i P_m$$

Dalton's law:

$$P_m = \sum_{i=1}^{k} P_i (T_m, V_m)$$

Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures. This is due to intermolecular forces that may be significant for real gases at high densities. For ideal gases, these two laws are identical and give identical results.

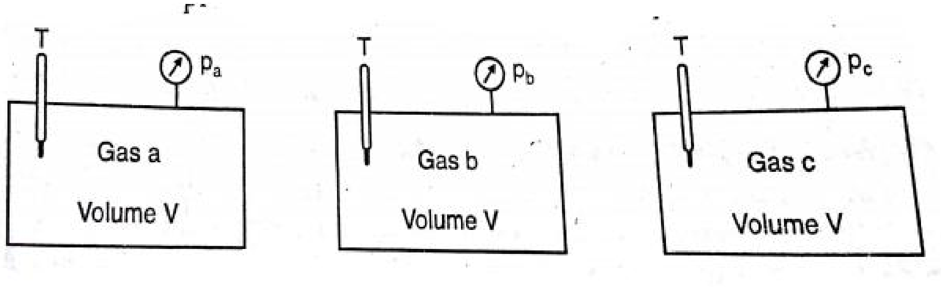
Now, consider placing each of the k gases in a separate container having the volume of the mixture at the temperature of the mixture. The pressure that results is called the component pressure, P_i' .



i^{th} gas

$T = T_m$ $\quad$ $V = V_m$

$P - P_i'$ $\quad$ $m - m_i$



Ideal-Gas Mixtures:

Ideal-Gas Mixtures For ideal gases, P_i' and V_i can be related to y_i by using the ideal-gas relation for both the components and the gas mixture:

$$P_i' = \frac{N_i R_u T_m}{V_m} \quad and \quad P_m = \frac{N_m R_u T_m}{V_m}$$

Note that the ratio of P_i' to P_m is

$$\frac{P_i'}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

Here $y_iP_{m\ =}$ is called the partial pressure (identical to the component pressure for ideal gases), and the quantity

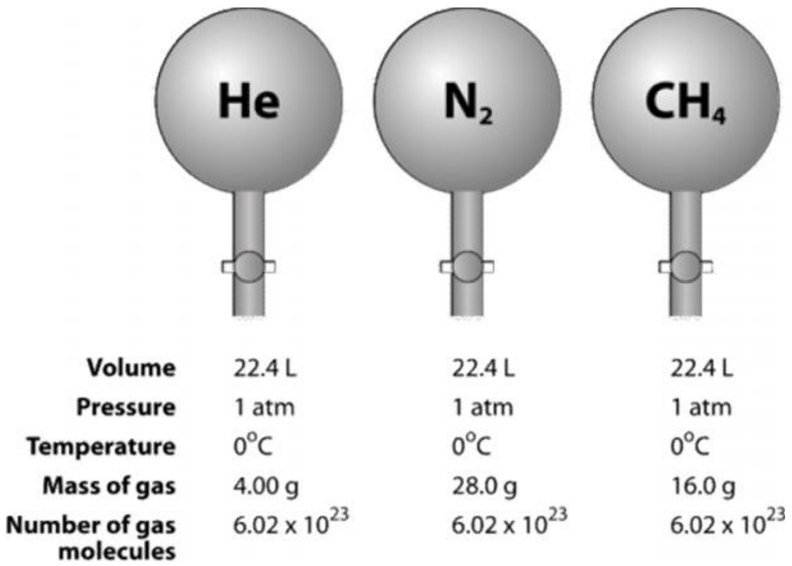
$y_iV_{m\ =}$ is called the partial volume (identical to the component volume for ideal gases).

Note: An ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.

Avogadro's Hypothesis: Equal volumes of all gases measured at the same temperature & pressure contain the same number of molecules or particles.

Avogadro's Law:

- At constant temperature & pressure, the volume of a gas is directly proportional to the number of moles of that gas.
  i.e., V α n, numbers of moles at constant temperature and pressure.
  V = a constant n.
  Or
  V/n = a constant



Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0°C	0°C	0°C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

PROPERTIES OF GAS MIXTURES:

IDEAL AND REAL GASES:

The extensive properties of a non reacting ideal or real-gas mixture: Just add the contributions of each component of the mixture. Then the total internal energy, enthalpy, and entropy of a gas mixture can be expressed, respectively, as

$$U_m = \sum_{i=1}^{k} U_i = \sum_{i=1}^{k} m_i u_i = \sum_{i=1}^{k} N_i \overline{u_i} \qquad (\text{kJ})$$

$$H_m = \sum_{i=1}^{k} H_i = \sum_{i=1}^{k} m_i h_i = \sum_{i=1}^{k} N_i \overline{h_i} \qquad (\text{kJ})$$

$$S_m = \sum_{i=1}^{k} S_i = \sum_{i=1}^{k} m_i s_i = \sum_{i=1}^{k} N_i \overline{s_i} \qquad (\text{kJ / K})$$

The internal energy, enthalpy, and entropy of a mixture per unit mass or per unit mole of the mixture can be determined by dividing the equations above by the mass or the mole number of the mixture (m_m or N_m). We obtain

$$u_m = \sum_{i=1}^{k} mf_i u_i \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^{k} y_i \bar{u}_i \quad (\text{kJ / kg or kJ / kmol})$$

$$h_m = \sum_{i=1}^{k} mf_i h_i \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^{k} y_i \bar{h}_i \quad (\text{kJ / kg or kJ / kmol})$$

$$s_m = \sum_{i=1}^{k} mf_i s_i \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^{k} y_i \bar{s}_i \quad (\text{kJ / kg} \cdot \text{K or kJ / kmol} \cdot \text{K})$$

Similarly, the specific heats of a gas mixture can be expressed as

$$C_{v,m} = \sum_{i=1}^{k} mf_i C_{v,i} \quad \text{and} \quad \bar{C}_{v,m} = \sum_{i=1}^{k} y_i \bar{C}_{v,i}$$

$$C_{p,m} = \sum_{i=1}^{k} mf_i C_{p,i} \quad \text{and} \quad \bar{C}_{p,m} = \sum_{i=1}^{k} y_i \bar{C}_{p,i}$$

These relations are applicable to both ideal- and real-gas mixtures. The properties or property changes of individual components can be determined by using ideal-gas or real-gas relations.
Ratio of specific heats k is given as

$$k_m = \frac{C_{p,m}}{C_{v,m}} = \frac{\bar{C}_{p,m}}{\bar{C}_{v,m}}$$

Properties per unit mass involve mass fractions $=mf_i$
Properties per unit mole involve mole fractions y_i.

- The relations given above are exact for ideal-gas mixtures, and approximate for real-gas mixtures. (In fact, they are also applicable to non reacting liquid and solid solutions especially when they form an “ideal solution.”)
- The only major difficulty associated with these relations is the determination of properties for each individual gas in the mixture.

Ideal-Gas Mixtures:

- The gases that comprise a mixture are often at a high temperature and low pressure relative to the critical-point values of individual gases.
- At that case, the gas mixture and its components can be treated as ideal gases with negligible error.
- Under the ideal-gas approximation, the properties of a gas are not influenced by the presence of other gases, and each gas component in the mixture behaves as if it exists alone at the mixture temperature T_m and mixture volume V_m.
- This principle is known as the Gibbs–Dalton law, which is an extension of Dalton’s law of additive pressures. Also, the h, u, c_v, and c_p of an ideal gas depend on temperature only and are independent of the pressure or the volume of the ideal-gas mixture.
- The partial pressure of a component in an ideal-gas mixture is simply $P_i = y_i P_m$,

- where P_m is the mixture pressure.
- Δu or Δh of the components of an ideal-gas mixture easily to calculate only knowledge of the initial and final temperatures.
- Δs is depends on the pressure or volume of the component as well as on its temperature.
- The entropy change of individual gases in an ideal-gas mixture during a process can be determined from

$$\Delta s_i = C_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$$

The entropy change of the mixture per mass of mixture is

$$\Delta s_m = \frac{\Delta s_m}{m_m} = \sum_{i=1}^{2} mf_i \Delta s_i = \sum_{i=1}^{2} mf_i \left(C_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)\right)$$

The entropy change of the mixture per mole of mixture is

$$\Delta \bar{s}_m = \frac{\Delta s_m}{N_m} = \sum_{i=1}^{2} {}_{iy} \Delta \bar{s}_i = \sum_{i=1}^{k} y_i \left(\bar{C}_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_u \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)\right)$$

In these last two equations,

$$P_{i,1} = y_{i,1} P_{m,1}$$

$$P_{i,2} = y_{i,2} P_{m,2}$$

ENGINEERING THERMODYNAMICS

Unit – VI

Objectives:

- To introduce the students to gas power cycles, vapour power cycles and refrigeration cycles

Syllabus:

Gas power cycles: Otto, diesel, dual combustion cycles, description and representation on P-v and T-s diagram, thermal efficiency, mean effective pressure on air standard basis- comparison of cycles, Brayton cycle

Vapour power cycles: Simple Rankine cycle, Refrigeration cycles: Bell Coleman cycle, vapour compression refrigeration system- performance evaluation.

Outcomes:

Students will be able to

- Evaluate thermal efficiency of Otto, diesel, dual cycle and Brayton cycle and they can represent on P-v and T-s diagrams
- Compare various gas power cycles
- Understand vapour power cycles
- Understand refrigeration cycles
- Evaluate performance of refrigeration cycles

- **Air-Standard Assumptions**

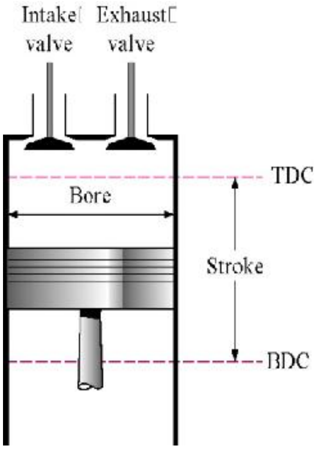
In our study of gas power cycles, we assume the working fluid is air, and the air undergoes a thermodynamic cycle even though the working fluid in the actual power system does not undergo a cycle.

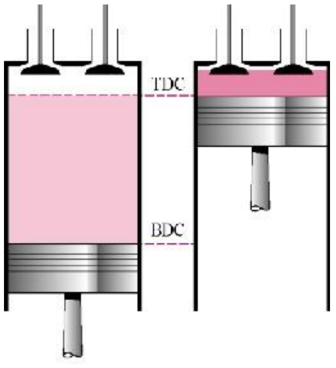
To simplify the analysis, we approximate the cycles with the following assumptions:

- The air continuously circulates in a closed loop and always behaves as an ideal gas.
- All the processes that make up the cycle are internally reversible.
- The combustion process is replaced by a heat-addition process from an external source.
- A heat rejection process that restores the working fluid to its initial state replaces the exhaust process.
- The cold-air-standard assumptions apply when the working fluid is air and has constant specific heat evaluated at room temperature (25^{o}C or 77^{o}F).

- **Terminology for Reciprocating Devices**

The following is some terminology we need to understand for reciprocating engines—typically piston-cylinder devices. Let's look at the following figures for the definitions of top dead center (TDC), bottom dead center (BDC), stroke, bore, intake valve, exhaust valve, clearance volume, displacement volume, compression ratio, and mean effective pressure.





(a) Displacement volume

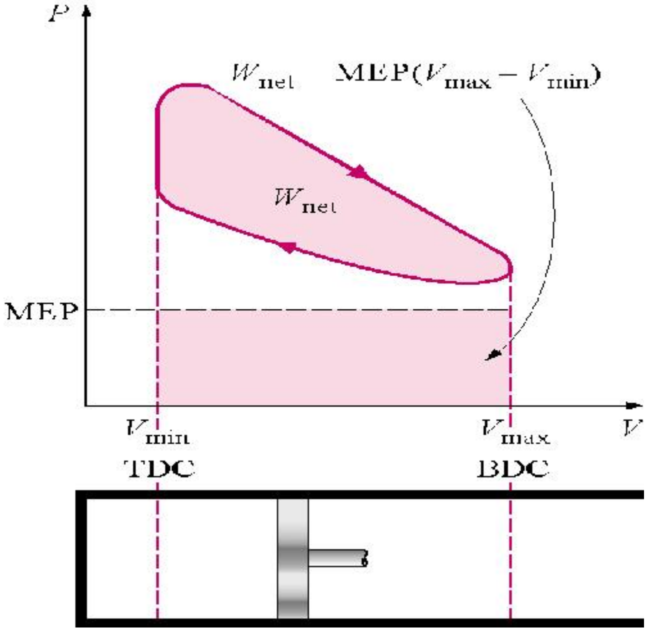
(b) Clearance volume

- The compression ratio r of an engine is the ratio of the maximum volume to the minimum volume formed in the cylinder.

$$r = \frac{V\max}{V\min} = \frac{V_{BDC}}{V_{TDC}}$$

- The mean effective pressure **(MEP*)*** is a fictitious pressure that, if it operated on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle.

$$MEP = \frac{W_{net}}{V_{\max} - V_{\min}} = \frac{w_{net}}{v_{\max} - v_{\min}}$$

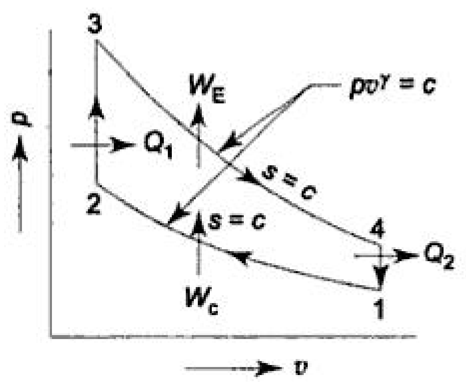


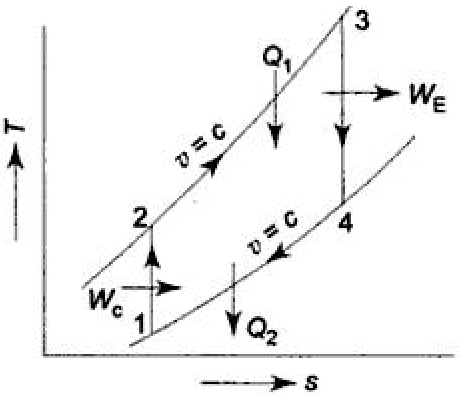
- **Otto Cycle (Constant Volume Cycle):**

This ideal heat engine cycle was proposed in 1862 by Bean de Rochas. In 1876 Dr. Otto designed an engine to operate on this cycle. The Otto engine immediately became so successful from a commercial stand point, that its name was affixed to the cycle used by it.

The ideal p - v and T-s diagrams of this cycle are shown in fig. In working out the air-standard efficiency of the cycle, the following assumptions are made:

(i) The working fluid (working substance) in the engine cylinder is air, and it behaves as a perfect gas, i.e., it obeys the gas laws and has constant specific heats.
(ii) The air is compressed adiabatically (without friction) according to law $pv^{\gamma} = C$
(iii) The heat is supplied to the air at constant volume by bringing a hot body in contact with the end of the engine cylinder.
(iv) The air expands in the engine cylinder adiabatically (without friction) during the expansion stroke.
(v) The heat is rejected from the air at constant volume by bringing a cold body in contact with the end of the engine cylinder.





Process 1→ 2 Isentropic compression
Process 2 → 3 Constant volume heat addition
Process 3 → 4 Isentropic expansion
Process 4 → 1 Constant volume heat rejection

Consider one kilogram of air in the engine cylinder at point (1). This air is compressed adiabatically to point (2), at which condition the hot body is placed in contact with the end of the cylinder. Heat is now supplied at constant volume, and temperature and pressure rise; this operation is represented by (2-3). The hot body is then removed and the air expands adiabatically to point (4). During this process, work is done on the piston. At point (4), the cold body is placed at the end of the cylinder. Heat is now rejected at constant volume, resulting in drop of temperature and pressure. This operation is represented by (4-1). The cold body is then removed after the air is brought to its original state (condition). The cycle is thus completed. The cycle consists of two constant volume processes and two reversible adiabatic processes. The heat is supplied during constant volume process (2-3) and rejected during constant volume process (4-1). There is no exchange of heat during the two reversible adiabatic processes (1-2) and (3-4).

The performance is often measured in terms of the cycle efficiency.

$$\eta_{th} = \frac{W_{net}}{Q_{in}}$$

Thermal Efficiency of the Otto cycle

$$\eta_{th} = \frac{W_{net}}{Q_{in}} = \frac{Q_{net}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

Now to find Q_{in} and Q_{out}.

Apply first law closed system, V = constant.

Heat supplied during constant volume operation (2-3), Heat rejected during constant volume operation (4-1) is

$$q_{in} = u_3 - u_2 = c_v(T_3 - T_2)$$
$$q_{out} = u_4 - u_1 = c_v(T_4 - T_1)$$

$$Q_{net,23} = \Delta U_{23}$$
$$Q_{net,23} = Q_{in} = mC_v(T_3 - T_2)$$

$$Q_{net,41} = \Delta U_{41}$$
$$Q_{net,41} = -Q_{out} = mC_v(T_1 - T_4)$$
$$Q_{out} = -mC_v(T_1 - T_4) = mC_v(T_4 - T_1)$$

The thermal efficiency becomes

$$\eta_{th,Otto} = 1 - \frac{Q_{out}}{Q_{in}}$$
$$= 1 - \frac{mC_v(T_4 - T_1)}{mC_v(T_3 - T_2)}$$

$$\eta_{th,Otto} = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)}$$
$$= 1 - \frac{T_1(T_4 / T_1 - 1)}{T_2(T_3 / T_2 - 1)}$$

Recall processes 1-2 and 3-4 are isentropic, so

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{\gamma-1} = \left(\frac{v_3}{v_4}\right)^{\gamma-1} = \frac{T_4}{T_3}$$

Since $V_3 = V_2$ and $V_4 = V_1$

$$\frac{T_2}{T_1} = \frac{T_3}{T_4}$$
$$or$$
$$\frac{T_4}{T_1} = \frac{T_3}{T_2}$$

The Otto cycle efficiency becomes

$$\eta_{th,Otto} = 1 - \frac{T_1}{T_2}$$

Since process 1-2 is isentropic,

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} = \left(\frac{1}{r}\right)^{\gamma-1}$$

Where the compression ratio is

$$r = \frac{v_{\max}}{v_{\min}} = \frac{v_1}{v_2}$$

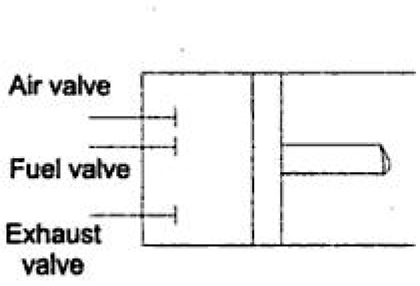
$$\eta_{th,\,Otto} = 1 - \frac{1}{r^{k-1}}$$

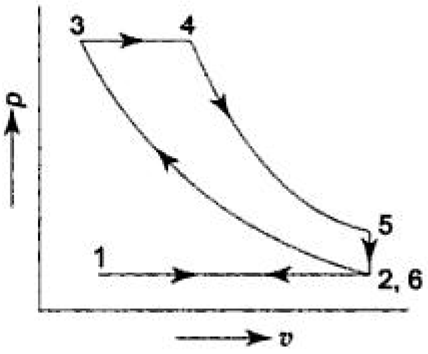
- **Air-Standard Diesel Cycle (or constant pressure cycle):**

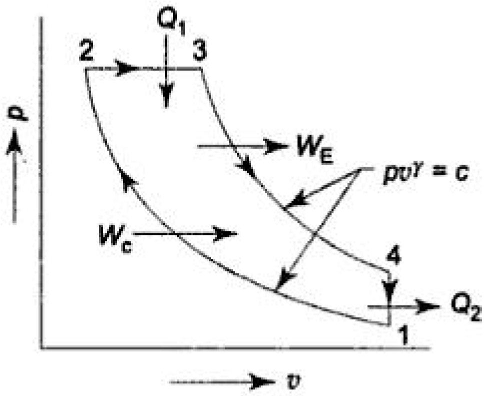
The air-standard Diesel cycle is the ideal cycle that approximates the Diesel combustion engine

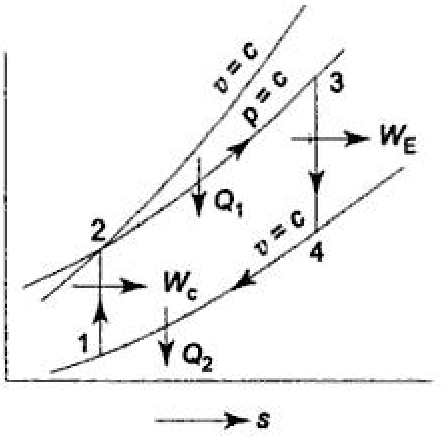
Process	Description
1-2	isentropic compression
2-3	Constant pressure heat addition
3-4	isentropic expansion
4-1	Constant volume heat rejection

The *P*-*v* and *T*-*s* diagrams are









$$Heat\ supplied = Q_1 = Q_{2-3} = mc_p(T_3 - T_2)$$

$$Heat\ \text{Rejected} = \text{Q}_2 = Q_{4-1} = mc_v(T_4 - T_1)$$

$$\text{Effieciency} = ¦ = 1 - \frac{Q_2}{Q_1} = 1 - \frac{mc_v(T_4 - T_1)}{mc_p(T_3 - T_2)} = 1 - \frac{(T_4 - T_1)}{¥(T_3 - T_2)}$$

The efficiency may be expressed terms of any two of the following.

$$Compression\ Ratio = r_k = \frac{v_1}{v_2}$$

$$Expansion\ Ratio = r_e = \frac{v_4}{v_3}$$

$$Cut - off\ \ ratio = r_c = \frac{v_3}{v_2}$$

$$r_k = r_e . r_c$$

Process 3-4

$$\frac{T_4}{T_3} = \left(\frac{v_3}{v_4}\right)^{¥-1} = \frac{1}{r_e^{¥-1}}$$

$$T_4 = T_3\left(\frac{v_3}{v_4}\right)^{¥-1} = T_3\frac{r_e^{¥-1}}{r_k^{¥-1}}$$

Process 2-3

$$\frac{T_2}{T_3} = \frac{p_2 v_2}{p_3 v_3} = \frac{v_2}{v_3} = \frac{1}{r_e}$$

$$T_2 = T_3\frac{1}{r_e}$$

Process 1-2

$$\frac{T_1}{T_2}=\left(\frac{v_2}{v_1}\right)^{\gamma-1}=\frac{1}{r_k^{\gamma-1}}$$

$$T_1=T_2\frac{1}{r_k^{\gamma-1}}=\frac{T_3}{r_c}\frac{1}{r_k^{\gamma-1}}$$

By subsisting T1,T2 and T4 in the expression of efficiency

$$\eta=1-\frac{T_3\dfrac{r_c^{\gamma-1}}{r_k^{\gamma-1}}-\dfrac{T_3}{r_c}\dfrac{1}{r_k^{\gamma-1}}}{\gamma\left(T_3-T_3\dfrac{1}{r_c}\right)}$$

$$\eta_{diesel}=1-\frac{1}{\gamma}\frac{1}{r_c^{\gamma-1}}.\frac{r_c^{\gamma-1}}{r_c-1}$$

- **Dual Cycle (mixed cycle/ limited pressure cycle):**

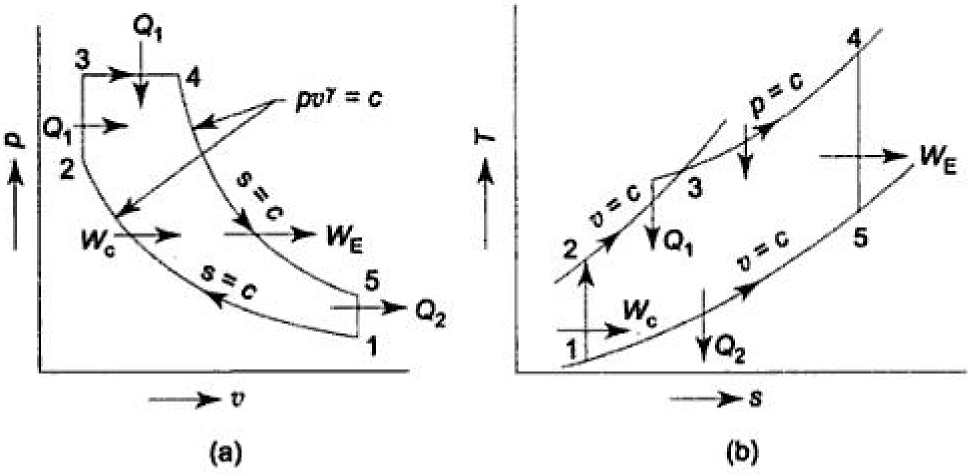
Process 1 → 2 Isentropic compression

Process 2 → 3Constant volume heat addition

Process 3 → 4 Constant pressure heat addition

Process 4 → 5 Isentropic expansion

Process 5→ 1 Constant volume heat rejection



Thermal Efficiency:

$$\text{where } r_c = {}^{v_3}\!/_{v_{2.5}} \text{ and} \sim = {}^{P_3}\!/_{P_2}$$

Note, the Otto cycle (r_c=1) and the Diesel cycle (a=1) are special cases:

$$¦_{Otto} = 1 - \frac{1}{r^{k-1}} \qquad ¦_{\substack{Diesel \\ const\, c_V}} = 1 - \frac{1}{r^{k-1}}\left[\frac{1}{k}\cdot\frac{\left(r_c^k - 1\right)}{\left(r_c - 1\right)}\right]$$

The use of the Dual cycle requires information about either:

i) The fractions of constant volume and constant pressure heat addition (common assumption is to equally split the heat addition), or

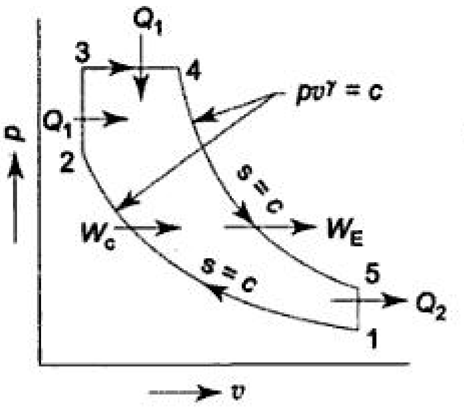
ii) Maximum pressure P_3.

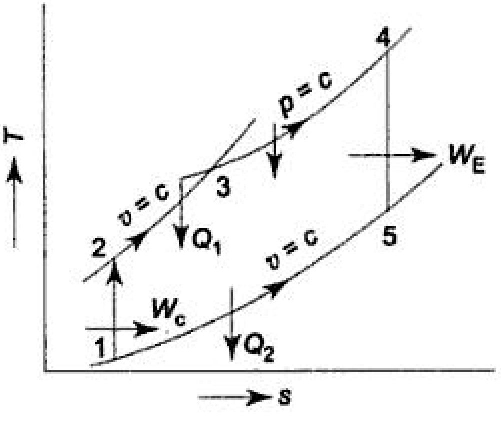
$$Q_1 = mc_v(T_3 - T_2) + mc_p\left(T_4 - T_3\right)$$
$$Q2 = mc_v(T_5 - T_1)$$

Here Q_1 -= heat input

Q_2 =Out put

$$¦ = 1 - \frac{Q_2}{Q_1} = 1 - \frac{mc_v(T_5 - T_1)}{mc_v(T_3 - T_2) + mc_p\left(T_4 - T_3\right)} = 1 - \frac{T_5 - T_1}{(T_3 - T_2) + ¥\left(T_4 - T_3\right)}$$





$$Compression\ Ratio = r_k = \frac{v_1}{v_2}$$

$$Expansion\ Ratio = r_e = \frac{v_4}{v_3}$$

$$cons\tan t - volume - pressure - ratio = r_p = \frac{p_3}{p_2}$$

$$r_k = r_c . r_e$$

$$r_e = \frac{r_k}{r_e}$$

$$process 3-4$$

$$r_c = \frac{v_4}{v_3} = \frac{T_4 p_3}{p_4 T_3} = \frac{T_4}{T_3}$$

$$T_3 = \frac{T_4}{r_c}$$

$$\Pr ocess 2-3$$

$$\frac{p_2 v_2}{T_2} = \frac{p_3 v_3}{T_3}$$

$$T_2 = T_3 \frac{p_2}{p_3} = \frac{T_4}{r_p r_c}$$

$$process - 1 - 2$$

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1} \right)^{\text{¥}-1} = \frac{1}{r_k^{\text{¥}-1}}$$

$$T_1 = \frac{T_4}{r_p . r_c . r_k^{\text{¥}-1}}$$

Process 4-5

$$T_1 = \frac{T_4}{r_p . r_c . r_k^{\text{¥}-1}}$$

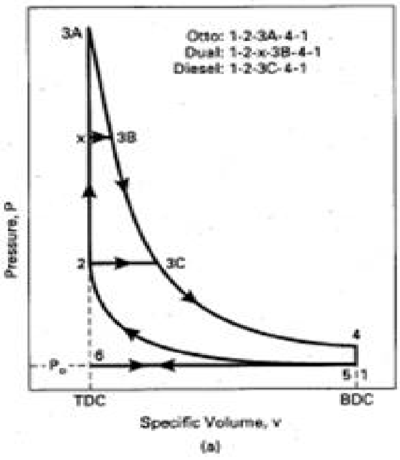
$$\frac{T_5}{T_4} = \left(\frac{v_4}{v_5} \right)^{\text{¥}-1} = \frac{1}{r_e^{\text{¥}-1}}$$

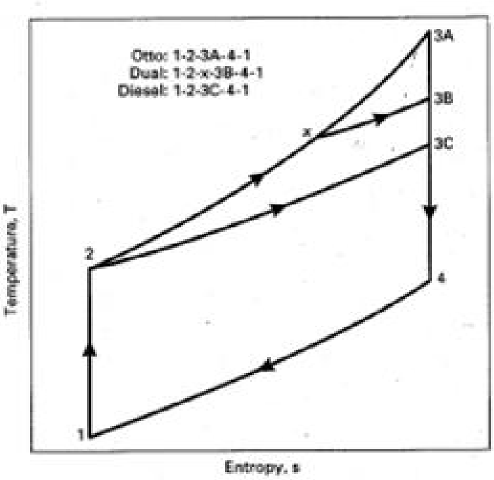
$$T_5 = T_4 \frac{r_c^{\text{¥}-1}}{r_k^{\text{¥}-1}}$$

SubtitlingT1, T2,T3 and T4values

$$\eta_{dual} = 1 - \frac{T_4 \dfrac{r_c^{\gamma-1}}{r_k^{\gamma-1}} - \dfrac{T_4}{r_p . r_c . r_k^{\gamma-1}}}{\left(\dfrac{T_4}{r_c} - \dfrac{T_4}{r_p r_c}\right) + \gamma\left(T_4 - \dfrac{T_4}{r_c}\right)} = 1 - \frac{1}{r_k^{\gamma-1}} \frac{r_p r_c^{\gamma-1}}{r_p - 1 + \gamma r_p \left(r_c - 1\right)}$$

- **Comparison of cycles:**
  - For the same inlet conditions P_1, V_1 and the same compression ratio P_2/P_1:

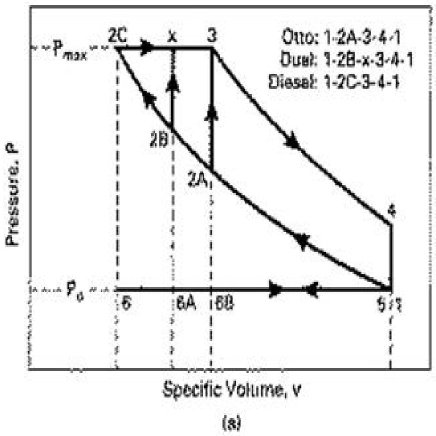


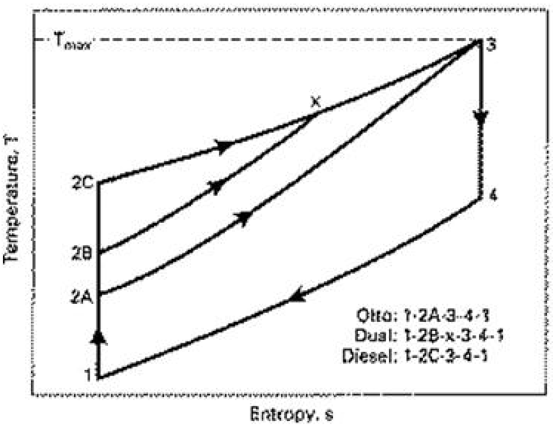


For the same initial conditions P_1, V_1 and the same compression ratio:

$$\eta_{Otto} > \eta_{Dual} > \eta_{Diesel}$$

  - For the same inlet conditions P_1, V_1 and the same peak pressure P_3:





For the same initial conditions P_1, V_1 and the same peak pressure P_3

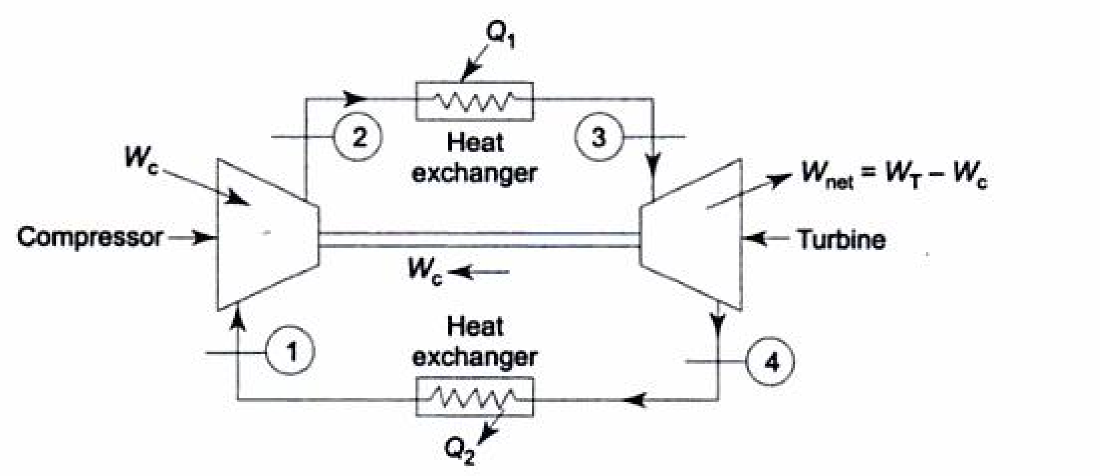
(Actual design limitation in engines):

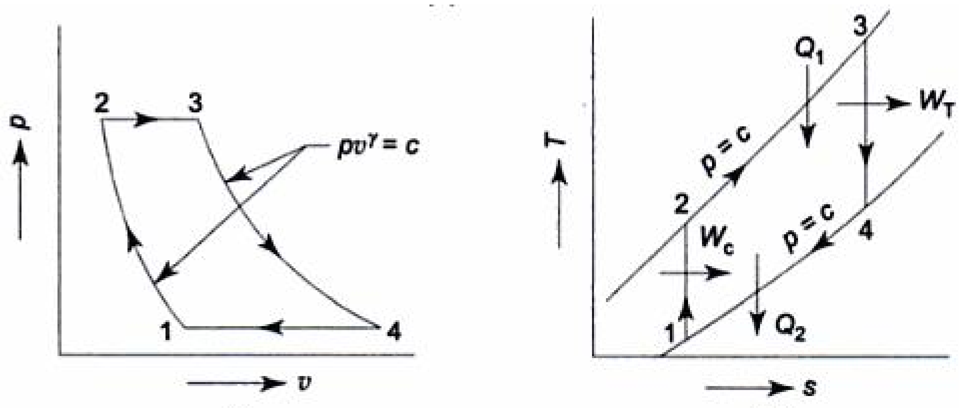
$$\eta_{Diesel} > \eta_{Dual} > \eta_{otto}$$

- **Brayton Cycle (or Joule cycle)**

The Brayton cycle is the air-standard ideal cycle approximation for the gas-turbine engine. This cycle differs from the Otto and Diesel cycles in that the processes making the cycle occur in open systems or control volumes. Therefore, an open system, steady-flow analysis is used to determine the heat transfer and work for the cycle.

We assume the working fluid is air and the specific heats are constant and will consider the cold-air-standard cycle.





(b) (c)

The closed cycle gas-turbine engine

The *T*-*s* and *P*-*v* diagrams for the

Closed Brayton Cycle

Process	Description
1-2	Isentropic compression (in a compressor)
2-3	Constant pressure heat addition
3-4	Isentropic expansion (in a turbine)
4-1	Constant pressure heat rejection

Thermal efficiency of the Brayton cycle

$$\boxed{\eta_{th,\,Brayton} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}}$$

Now to find Q_{in} and Q_{out}.

Apply the conservation of energy to process 2-3 for P = constant (no work), steady-flow, and neglect changes in kinetic and potential energies.

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{m}_2 h_2 + \dot{Q}_{in} = \dot{m}_3 h_3$$

The conservation of mass gives

$$\dot{m}_{in} = \dot{m}_{out}$$

$$\dot{m}_2 = \dot{m}_3 = \dot{m}$$

For constant specific heats, the heat added per unit mass flow is

$$\dot{Q}_{in} = \dot{m}(h_3 - h_2)$$

$$\dot{Q}_{in} = \dot{m} C_p (T_3 - T_2)$$

$$q_{in} = \frac{\dot{Q}_{in}}{\dot{m}} = C_p (T_3 - T_2)$$

The conservation of energy for process 4-1 yields for constant specific heats

$$\boxed{\begin{aligned} \dot{Q}_{out} &= \dot{m}(h_4 - h_1) \\ \dot{Q}_{out} &= \dot{m} C_p (T_4 - T_1) \end{aligned}}$$

$$q_{out} = \frac{\dot{Q}_{out}}{\dot{m}} = C_p (T_4 - T_1)$$

The thermal efficiency becomes

$$\eta_{th,\,Brayton} = 1 - \frac{\dot{Q}_{out}}{\dot{Q}_{in}} = 1 - \frac{q_{out}}{q_{in}}$$
$$= 1 - \frac{C_p(T_4 - T_1)}{C_p(T_3 - T_2)}$$

$$\boxed{\eta_{th,\,Brayton} = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)}}$$
$$= 1 - \frac{T_1(T_4 / T_1 - 1)}{T_2(T_3 / T_2 - 1)}$$

Recall processes 1-2 and 3-4 are isentropic, so

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$
$$\frac{T_3}{T_4} = \left(\frac{p_3}{p_4}\right)^{\frac{\gamma-1}{\gamma}}$$

Since $P_3 = P_2$ and $P_4 = P_1$,

$$\frac{T_2}{T_1} = \frac{T_3}{T_4}$$
$$or$$
$$\frac{T_4}{T_1} = \frac{T_3}{T_2}$$

The Brayton cycle efficiency becomes

$$\eta_{th,\,Brayton} = 1 - \frac{T_1}{T_2}$$

Since process 1-2 is isentropic,

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = r_p^{\frac{\gamma-1}{\gamma}}$$
$$\frac{T_1}{T_2} = \frac{1}{r_p^{\frac{(\gamma-1)}{\gamma}}}$$

Where the pressure ratio is $r_p = P_2/P_1$ and

$$\boxed{\eta_{th,\,Brayton} = 1 - \frac{1}{r_p^{(\gamma-1)/\gamma}}}$$

SIMPLE RANKINE CYCLE

Rankine Cycle: The simplest way of overcoming the inherent practical difficulties of the Carnot cycle without deviating too much from it is to keep the processes 1-2 and 2-3 of the latter unchanged and to continue the process 3-4 in the condenser until all the vapour has been converted into liquid water. Water is then pumped into the boiler upto the pressure corresponding to the state 1 and the cycle is completed. Such a cycle is known as the Rankine cycle. This theoretical cycle is free of all the practical limitations of the Carnot cycle.

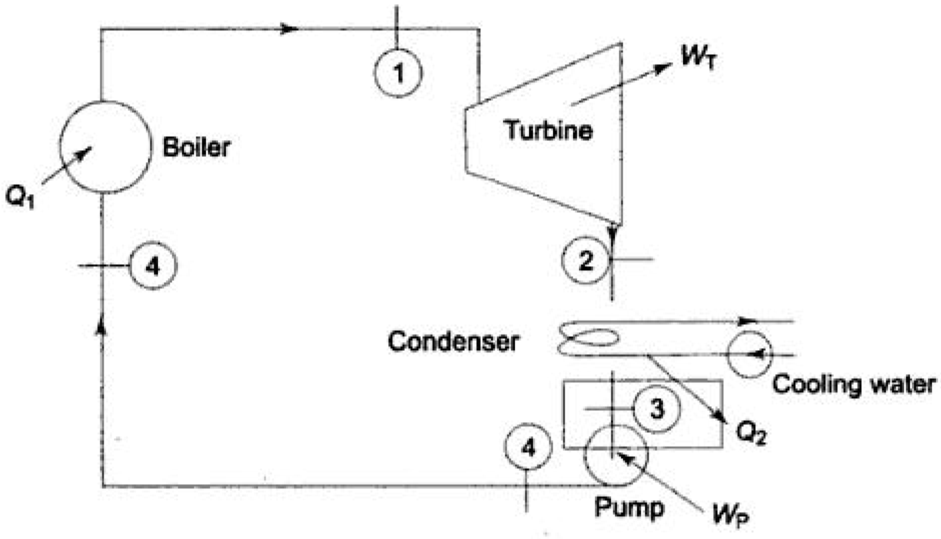


Figure (a) shows the schematic diagram for a simple steam power cycle which works on the principle of a Rankine cycle.

The Rankine cycle comprises the following processes.

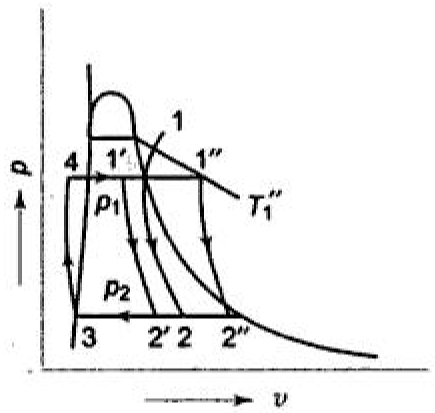
Process 1-2: Constant pressure heat transfer process in the boiler

Process 2-3: Reversible adiabatic expansion process in the steam turbine

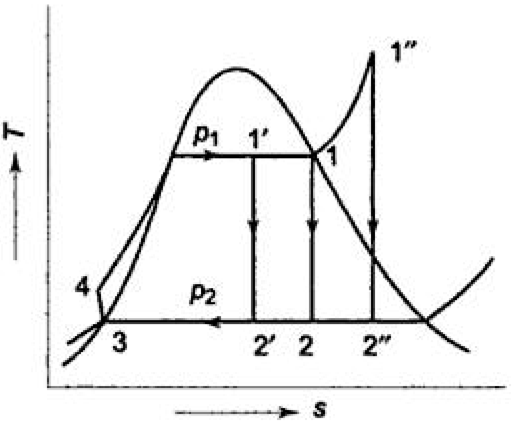
Process 3-4: Constant pressure heat transfer process in the condenser and

Process 4-1: Reversible adiabatic compression process in the pump.

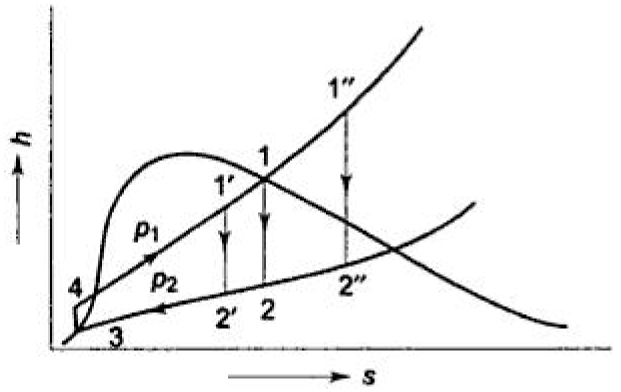
Figure (b) represents the T-S diagram of the cycle.



(a)



(b)



The numbers on the plots correspond to the numbers on the schematic diagram. For any given pressure, the steam approaching the turbine may be dry saturated (state 2), wet (state 2^1) or superheated (state 2^{11}), but the fluid approaching the pump is, in each case, saturated liquid (state 4). Steam expands reversibly and adiabatically in the turbine from state 2 to state 3 (or 2^1 to 3^1 or 2^{11} to 3^{11}), the steam leaving the turbine condenses to water in the condenser reversibly at constant pressure from state 3 (or 3^1, or 3^{11}) to state 4. Also, the water is heated in the boiler to form steam reversibly at constant pressure from state 1 to state 2 (or 2^1 or 2^{11})

Applying SFEE to each of the processes on the basis of unit mass of fluid and neglecting changes in KE & PE, the work and heat quantities can be evaluated

For 1kg of fluid, the SFEE for the boiler as the CV, gives,

$h_4 + Q_1 = h_1$ i.e., $Q_1 = h_1 - h_4$ --- (1)

SFEE to turbine, $h_1 = W_T + h_2$ i.e., $W_T = h_1 - h_2$ --- (2)

SFEE to condenser, $h_2 = Q_2 + h_3$ i.e., $Q_L = h_2 - h_3$ --- (3)

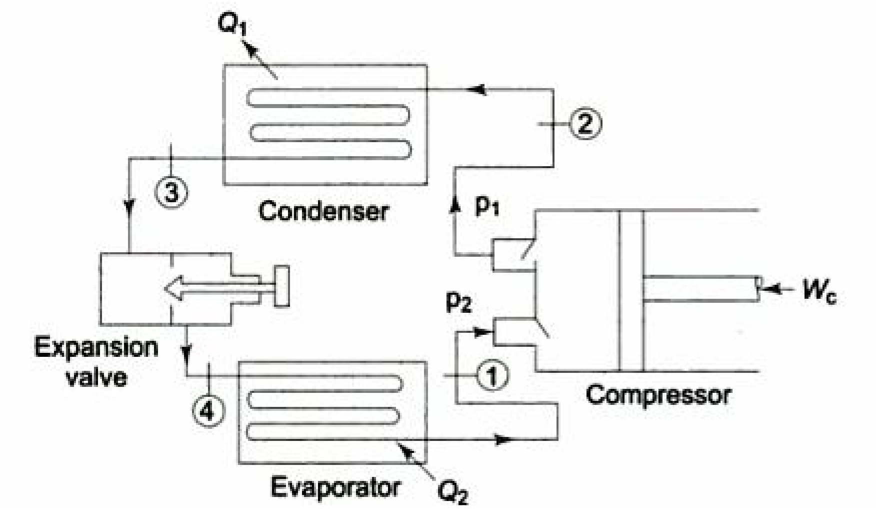
SFEE to pump, $h_3 + W_P = h_4$ i.e., $W_P = h_4 - h_3$ --- (4)

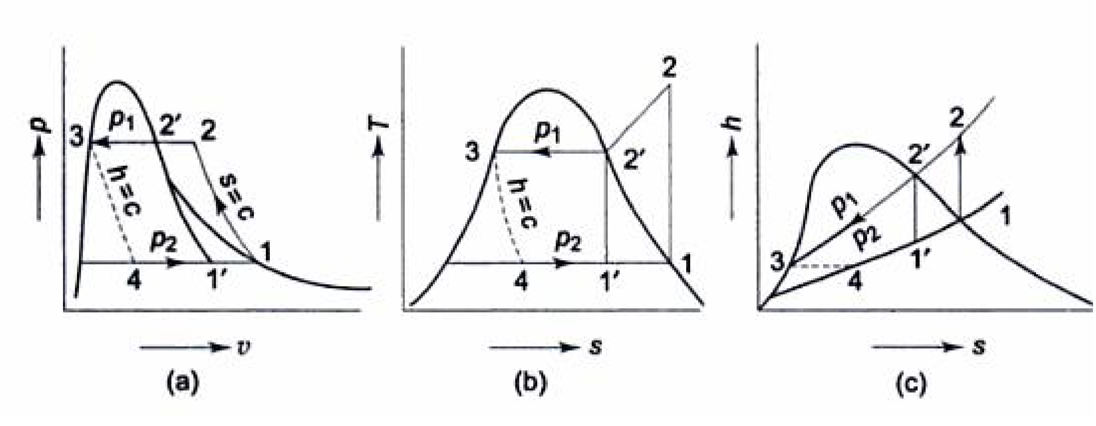
The efficiency of Rankine cycle is $\eta = \frac{W_{net}}{Q_1}$

The efficiency of Rankine cycle is $\boxed{\eta = \frac{W_{net}}{Q_1} = \frac{W_T - W_p}{Q_1} = \frac{(h_1 - h_2) - (h_4 - h_3)}{h_1 - h_4}}$

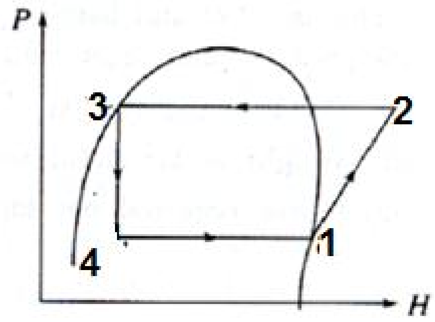
VAPOUR COMPRESSION REFRIGERATION SYSTEM

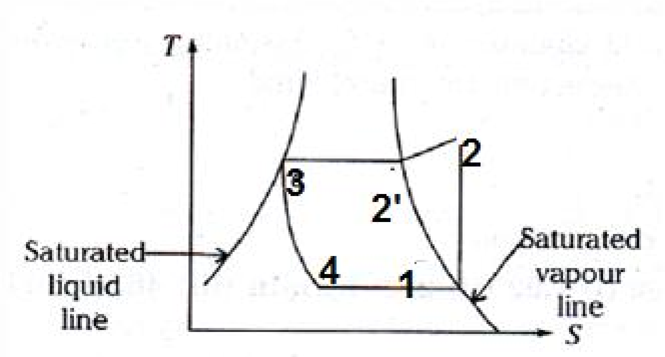
In vapour compression system, the refrigerants used are ammonia, carbon dioxide, freons etc. the refrigerants alternately undergoes condensation and evaporation during the cycle. When refrigerant enters the evaporator it will be in liquid state and by absorbing latent heat it become vapours. Thus the C.O.P of this system is always much higher that air refrigeration systems.





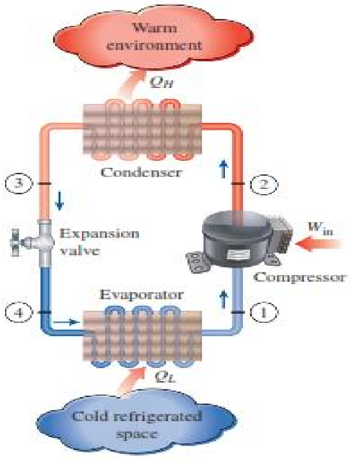
VAPOUR COMPRESSION REFRIGERATION SYSTEM





P-V Diagramv

T-S Diagram



The various processes are

Process 1-2 .

The vapour refrigerant entering the compressor is compressed to high pressure and temperature in a isentropic manner.

Process 2-3.

This high pressure and high temperature vapour then enters a condenser where the temperature of the vapour first drops to saturation temperature and subsequently the vapour refrigerants condenses to liquid state.

- **Process 3-4.**

This liquid refrigerant is collected in the liquid storage tank and later on it is expanded to low pressure and temperature by passing it through the throttle valve. At point d we have low temperature liquid refrigerant wuitn small amount of vapour.

• **Process 4-1**.

This low temperature liquid then enters the evaporator where it absorbs heat from the space to be cooled namely the refrigerator and become vapour.

Compressor work Wc = h_2-h_1 kJ/kg

Condenser work = h_2-h_3 kJ/kg

Expansion value = h_3=h_4 kJ/kg

h_{f2}= h_{f1}+(x_4 h_{fg4})

$$x_4 = \frac{\left(hf_2 - hf_1\right)}{hfg_4}$$

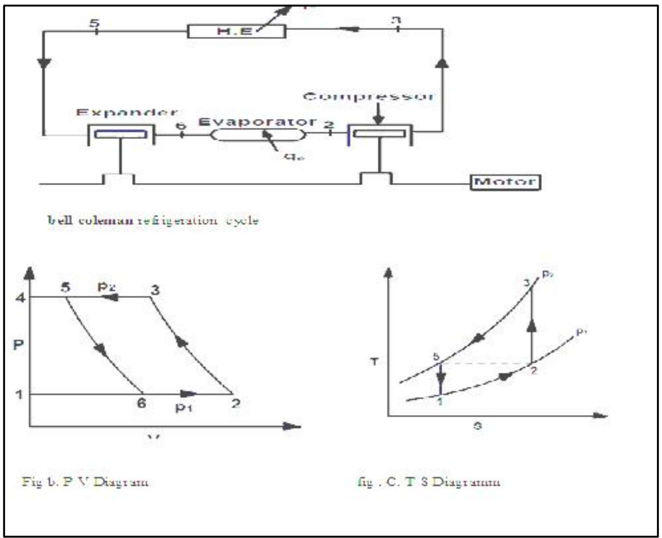
Evaporator $Q_2 = h_4 - h_1$ kJ/kg

Refrigerant effect is amount of heat removed from the surrounding per unit mass flow rate of refrigerant

Coefficient of performance
$$\boxed{cop = \frac{Q_2}{w_c} = \frac{h_1 - h_4}{h_2 - h_1}}$$

Air Refrigeration System And Bell-Coleman Cycle Or Reversed Brayton Cycle

The components of the air refrigeration system are shown in Fig.(a). In this system, air is taken into the compressor from atmosphere and compressed. The hot compressed air is cooled in heat exchanger upto the atmospheric temperature (in ideal conditions). The cooled air is then expanded in an expander. The temperature of the air coming out from the expander is below the atmospheric temperature due to isentropic expansion. The low temperature air coming out from the expander enters into the evaporator and absorbs the heat. The cycle is repeated again. The working of air refrigeration cycle is represented on p-v and T-s diagrams in Fig.(b) and (c).



bell coleman refrigeration cycle

Fig b. P V Diagram

fig . C. T S Diagramm

Process 1-2 represents the suction of air into the compressor.

Process 2-3 represents the isentropic compression of air by the compressor.

Process 3-5 represents the discharge of high pressure air from the compressor into the heat exchanger. The reduction in volume of air from v3 to v5 is due to the cooling of air in the heat exchanger. Process 5-6 represents the isentropic expansion of air in the expander.

Process 6-2 represents the absorption of heat from the evaporator at constant pressure

Assumptions:

1) The compression and expansion processes are reversible adiabatic processes.

2) There is a perfect inter-cooling in the heat exchanger.

3) There are no pressure losses in the system.

$$cop = \frac{Net\ refrigeration\ effect}{Net\ work\ supplied}$$

Net refrigeration effect

Net work supplied

Work done per kg of air for the isentropic compression process 2-3 is given by,

$$W_c = C_p(T_3 - T_2)\ \text{kJ/kg K}$$

Work developed per kg of air for the isentropic expansion process 5-6 is given by,

$$W_E = C_p(T_5 - T_6)\ \text{kJ/kg K}$$

Net work required $W_{net} = (W_C - W_E) = (C_p(T_3 - T_2)) - (C_p(T_5 - T_6))$ kJ/kg K

Net refrigerating effect per kg of air is given by,

$R_{net} = C_p (T_2 - T_6)$ kJ/kg K

$$cop = \frac{c_p\left(T_2 - T_6\right)}{c_p(T_3 - T_2) - \left(T_5 - T_6\right)}$$

For perfect inter-cooling, the required condition is $T_5 = T_2$

$$\boxed{cop = \frac{c_p\left(T_2 - T_6\right)}{c_p(T_3 - T_2) - \left(T_2 - T_6\right)}}$$

$$\frac{T_3}{T_2} = {\frac{p_1}{p_2}}^{\frac{\text{¥}-1}{\text{¥}}} \rightarrow \qquad \frac{T_5}{T_6} = {\frac{p_2}{p_1}}^{\frac{\text{¥}-1}{\text{¥}}} \qquad \frac{T_3}{T_2} = \frac{T_5}{T_6} \qquad \frac{T_6}{T_5} = \frac{T_2}{T_3}$$

or $T_5 = T_2$

Performance of The system $\boxed{cop = \frac{T_2}{T_3 - T_2}}$