Chapter 1

1.1 Definition

The word thermodynamics stems from the Greek words *therme* (heat) and *dynamis* (force/power), which is most descriptive of the early efforts to convert heat into power: the capacity of hot bodies to produce work.

Today, Thermodynamics is defined as the study of energy, its forms and transformations and the interactions of energy with matter. Hence, thermodynamics is concered with

- the concept of energy
- the law that governs the conversion of one form of energy into another
- the properties of the working substances or the media used to obtain the energy conversion.

1.2 Value of Energy to Society

The availability of energy and people's ability to harness that energy in useful ways have transformed our society. A few hundred years ago, the greatest fraction of the population struggled to subsist by producing food for local consumption. Now, in many countries a small fraction of the total work force produces abundant food for the entire population, and much of the population is freed for other jobs. We are able to travel great distances in short times by using a choice of transport means; we can communicate instantaneously with persons anywhere on earth; and we control large amounts of energy at our personal whim in the form of automobiles, electric tools and appliances, and comfort conditioning in our dwellings.

It is very hard to imagine the present life without electricity and other forms of energy. The energy available and consumed data exhibit the perspective picture of the economic condition and scope and the level of advancement of living people's civilization.

1.3 Macroscopic versus Microscopic Viewpoint

It is well-known that a substance consists of a large number of particles called molecules. The properties of the substance naturally depend on the behavior of these particles.

There are two points of view from which the behavior of matter can be studied: the macroscopic and the microscopic approach.

a) Macroscopic Approach

This is the approach to the thermodynamics is concerned with gross or overall behavior. The properties of the substance/matter is considered without taking into account the events occurring at the molecular level.

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 behavior of the gas particles to determine the pressure in the container. It would be sufficient to attach a pressure gauge to the container. Hence, instruments are used to find the value of the thermodynamic properties.

This macroscopic approach to the study of thermodynamic that does not require knowledge of the behavior of individual particles is called **classical thermodynamics**. It provides a direct and easy way to the solution of engineering problems. The values of the properties of the systems are their average values like pressure, temperature etc.

b) Microscopic approach

A more elaborate approach, based on the average behavior of large groups of individual particles is called microscopic approach or **statistical thermodynamics**. The properties like velocity, momentum, impulse etc. are studied by this approach. It required advanced statistical and mathematical method since they are not easily measured by instruments.

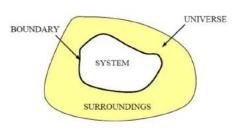
1.4 Concept and Definitions

1.4.1 System and Surrounding

Universe: is defined as the totality of matter that exists.

A system and its surroundings together comprise a universe.

System: is a quantity of matter or a region in space selected for examination and analysis (study). The system is a specified region wherein changes due to transfers of mass and energy or both are to be studied.

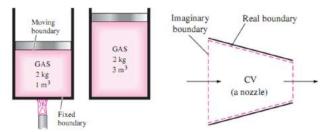


It is not necessary that the volume or shape of the system should remain fixed.

Surrounding: It is the part of universe external to the system which strongly interacts with the system under study.

Boundary: The real or imaginary surface that separates system from its surroundings is called boundary. The boundary of a system can be fixed or movable. It is a contact surface shared by both the system and surrounding.

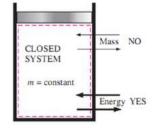
Note: all transfers of mass and energy between the system and surroundings are evaluated at the boundary.



The thermodynamic system may be classified into the following three groups: (a) Closed system; (b) Open system; and (c) Isolated system.

a) Closed system

A system with fixed amount of matter (mass) i.e. no matter (mass) can cross its boundary but the energy, in the form of heat or work can cross the boundary. It is also referred to as control mass (CM).

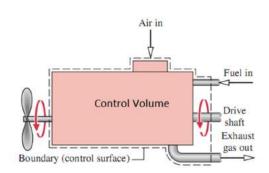


b) Isolated System

If neither mass nor energy is allowed to cross the boundary of a system is called an isolated system. It is a special type of closed system that does not interact in any way with its surrounding. E.g. any closed rigid insulated box.

c) Open system

If both mass and energy cross the boundary of a system, it is called open system. An open system permits both mass and energy cross the boundaries and the mass within the system may not remain constant. It is also called **control volume (CV)**.



Note: When the terms control mass and control

volume are used the system boundary is often referred to as a control surface.

1.4.2 Thermodynamic Property

The parameter to define the characteristic of system is called thermodynamic property. A thermodynamic property is a macroscopic characteristic of a system such as mass, volume, energy, pressure, and temperature to which a numerical value can be assigned at a given time without knowledge of the previous behavior (history) of the system.

The thermodynamic properties of a system may be divided into the following two general classes.

a) Extensive properties

A property is called extensive if its value for an overall system is the sum of its values for the parts into which the system is divided i.e. it is additives. The value of a property is proportional to the mass of the system. Mass, volume, energy, and several other properties introduced later are extensive. Extensive properties depend on the size or extent of a system. The extensive properties of a system can change with time.

b) Intensive properties

If the value of a property is independent of the size or extent of a system i.e. independent of the mass of the system, it is referred as intensive properties. Intensive properties are not additive in the sense previously considered. It may vary from place to place within the system at any moment. Thus, intensive properties may be functions of both position and time.

The ratio of an extensive property 'X' to the mass 'm' is called the specific value 'X/m' of that property. Thus, v=V/m is the specific volume, specific total energy (e = E/m).

Generally, uppercase letters are used to denote extensive properties (with mass 'm' being a major exception), and lowercase letters are used for intensive properties (with pressure 'P' and temperature 'T' being the obvious exceptions).

1.4.3 Thermodynamic state and Thermodynamic Equilibrium

The word state refers to the condition of a system as described by its properties such as pressure, volume, temperature, mass etc. 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. Hence, each unique condition of system is called a state. State is the condition of the system as all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition.

On the basis of the above discussion we can determine if a given variable is a property or not by applying the following tests:

- (a) A variable is a property if, and only if, it has a single value at each equilibrium state.
- (b) A variable is a property if, and only if, the change in its value between any two prescribed equilibrium states is single valued.

Thermodynamics deals with equilibrium states. The word equilibrium implies a state of balance. In an equilibrium state there are no unbalanced potentials (or driving forces) within a system. For a system, the properties describing the state will be constant if the system is not allowed to interact with the surroundings or it the system is allowed to interact completely with unchanging surroundings. Such a state is termed an equilibrium state and the properties are equilibrium properties.

A system will be in a state of thermodynamic equilibrium, if the condition for the following three types of equilibrium are satisfied

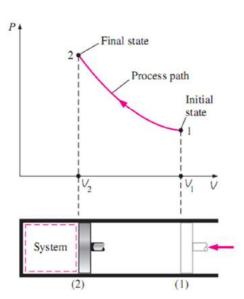
- a) Mechanical equilibrium: a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time.
- b) Thermal equilibrium: a system is in thermal equilibrium if the temperature is the same throughout the entire system
- c) Chemical equilibrium: a system is in chemical equilibrium if its chemical composition does not change with time, that is, no chemical reactions occur

1.4.4 Thermodynamic Process 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.

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

viewed as a sufficiently slow process and also called reversible process. It should be pointed out that a quasi-equilibrium process is an idealized process and is not a true representation of an actual process. But many actual processes closely approximate it. It is important because:

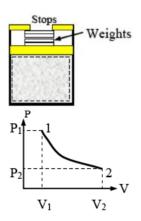


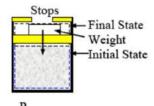
- a) they are easy to analyze
- b) serves as standards to which actual process can be compared.

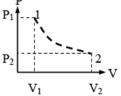
Let us consider a system of gas contained in a cylinder. The system initially is in equilibrium state, represented by the properties P₁, V₁, T₁. The weight on the piston just balances the upward force exerted by the gas. If the weights are removed one by one very slowly from the top of the piston, at any instant of the upward travel of the piston, considering gas system is isolated, every state passed through by the system will be an equilibrium state. Such a process, which is locus of all the equilibrium points passed through by the system, is known as quasi-static or quasi-equilibrium process. A quasi-static process is thus a succession of equilibrium states and represented by a continuous line.

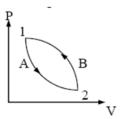
If the weight is single and is removed, there will be an unbalanced force between the system and the surroundings, and under gas pressure, the piston will move up till it hits the stops. The system again comes to an equilibrium state, being described by the properties P₂, V₂, T₂. Thus, the intermediate states passed through by the system are non-equilibrium states which cannot be described by thermodynamic properties. such process is called non quasi-equilibrium process or irreversible process denoted by a dashed line between initial and final states.

When a process or processes are performed on a system in such a way that the final state is identical with the initial state, it is the known as a thermodynamic cycle or cyclic process. In Figure, 1-A-2 and 2-B-1 are processes whereas 1-A-2-B-1 is a thermodynamic cycle.









1.4.5 Some Common Properties:

a) Pressure:

It is defined as the normal force exerted per unit area.

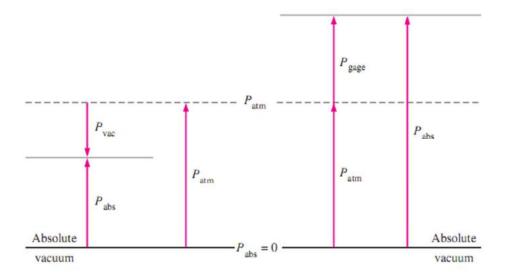
With the restriction that area over which the force is applied must not smaller than some minimum value a, the mathematical definition of the local pressure is

$$P = \lim_{\Delta A \to a} \frac{\Delta F_N}{\Delta A} \left(\frac{N}{m^2}, Pa \right)$$

The actual pressure at a given position is called **absolute pressure** and it is measured relative to absolute vacuum i.e. absolute zero pressure. The difference between absolute pressure and local atmospheric pressure is called **gauge pressure**. Gauge pressure may be positive or negative. Pressure below atmospheric pressure is called **vacuum pressure**.

Pabs = Patm+ Pgauge

Pvac = Patm - Pabs



Pressure Variation with depth

For fluids whose density changes significantly with elevation, a relation for the variation of pressure with elevation can be obtained by

$$\frac{dP}{dz} = -\rho g$$

The negative sign is due to our taking the positive z direction to be upward so that dP is negative when dz is positive since pressure decreases in an upward direction. When the variation of density with elevation is known, the pressure difference between points 1 and 2 can be determined by integrating

$$P_1 = P_{atm}$$

$$P_1 = P_{atm}$$

$$P_1 = P_{atm}$$

$$\Delta P = P_2 - P_1 = -\int_1^2 \rho g dz = -\rho g(z_1 - z_2) = \rho g h$$

$$P_2 - P_{atm} = \rho g h = P_{gauge}$$

Manometer

A manometer is a device to measure the pressure difference based on the principle of variation of pressure with depth.

$$P_{aas} - P_{atm} = \rho g L$$

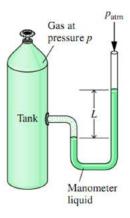
where, ρ is the density of the manometer liquid and L is the pressure head.

b) Specific Volume:

The specific volume (v) of a substance is defined as the volume per unit mass and is measured in m^3/kg . Thus, mathematical definition of specific volume is

$$v=V/m$$

Hence, specific volume is the reciprocal of the density, i.e., $v=1/\rho$



c) Temperature

It is an intensive thermodynamic property, which determines the degree of hotness or the level of heat intensity of a body. A body is said to be at a high temperature or hot, if it shows high level of heat intensity in it. Similarly, a body is said to be at a low temperature or cold, if it shows a low level of heat intensity.

The instrument used to measure the temperature is called thermometer. For most **Temperature Scales:**

Temperature Scales enable us to use a common basic for temperature measurements. All temperature scales are based on some easily reproducible states such as the freezing and boiling point of water.

The two scales (Kelvin and Rankin scale) most useful in thermodynamics are so called absolutes scales. The absolute scale for SI is the Kelvin scale. This scale is a one point scale based on the second law of thermodynamics. The single point is the triple point of water, where ice, liquid water, and water vapor coexist in a closed system in the absence of air. Rankin scale is related to Kelvin scale by

 $1.8^{\circ}R = 1K$

Two other commonly used scales are the Fahrenheit scale and the Celsius scale.

1.4.6 Equality of Temperature and Zeroth Law of thermodynamics

The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. It serves as a basis for the validity of temperature measurement.

Chapter II. Properties of Pure Substances

Pure substance and state postulate

A pure substance is a system which is:

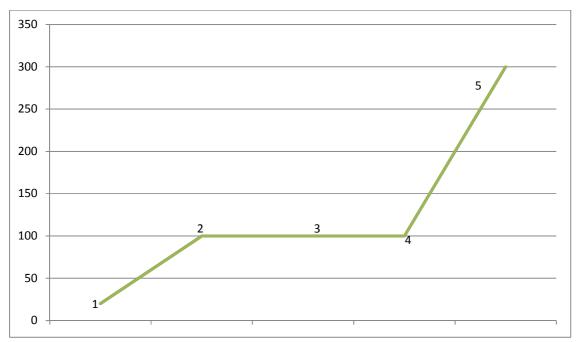
- 1. HOMOGENOUS IN CHEMICAL COMPOSITION: Same ratio of chemical elements throughout the system.
- 2. HOMOGENEOUS IN CHEMICAL AGGREGATION: Elements are combined chemically in a same way.
- 3. INVARIABLE IN CHEMICAL AGGREGATION: Chemical aggregation does not change with time.

$$H_2 + O(g)$$
 $H_2 O(g)$ $H_2 O(g)$ $H_2 O(g)$ $H_2 O(I)$

- Not a pure substance
 In the upper part of the system, the hydrogen and oxygen are not combined chemically, whereas, in the lower part of the system, they are combined in the form of water.
- Not a pure substance
 The system consists of
 uncombined hydrogen and
 oxygen gas in the atomic
 ratio 1:1 in the upper part,
 and water in the lower part.
- Pure substance

According to the state postulate of a pure substance, "The state of a simple compressible pure substance is defined by two independent properties." For example, if the temperature and specific volume of a superheated steam are specified, the state of the system is determined.

Vapor-Liquid-Solid Phase Equilibrium in a Pure Substance



Along Y-axis: Temperature (°C)

Along X-axis: Specific volume (m³/kg)

Consider a piston-cylinder assembly consisting of 1 kg of water contained with a pressure of 1 atmosphere or 101.3 kPa and the initial temperature being 20 °C. Heat is transferred to the cylinder while pressure is kept constant.

- As heat is transferred to the water, the temperature increases appreciably, the specific volume increases slightly and the pressure remains constant.
- Once the temperature reaches 100 °C, additional heat transfer results in a change of phase (liquid becomes vapour) during which both pressure and temperature remain constant but the specific volume increases appreciably.

• When the last drop of liquid has vaporized, further heat transfer results in both an increase in both temperature and specific volume of the vapor.

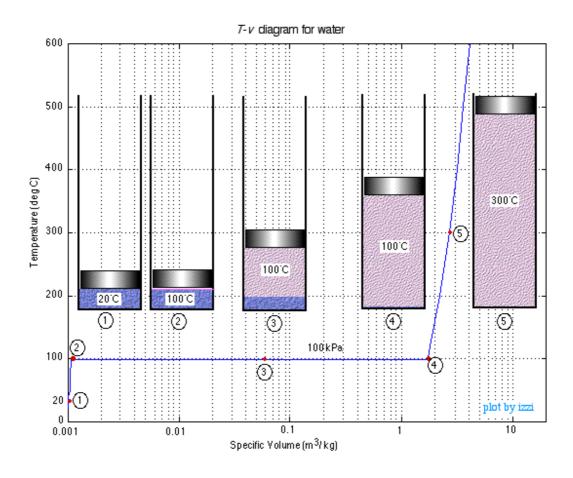
State 1: sub cooled liquid or compressed liquid

State 2: saturated liquid

State 3: mixture of liquid and vapor

State 4: saturated vapor

State 5: superheated vapor



Some Definitions

- If a substance exists as liquid at the saturation temperature and pressure it is called saturated liquid.
- If the temperature of the liquid is lower than the saturation temperature for the existing pressure, it is called either a **sub cooled liquid** or a **compressed liquid**.

• Quality indicates the mass fraction of vapour in a liquid vapour mixture.

$$quality(x) = \frac{mg}{mg + ml} = \frac{mg}{m}$$

mg = mass of vapor phase

ml = mass of liquid phase

m = total mass

•
$$0 \le x \ge 1$$

- Moisture content is defined as the ratio of the mass of liquid to the total mass.
- If a substance exists as vapour at the saturation temperature, it is called saturated vapour or sometimes dry saturated vapour to indicate the 100% quality.
- When the vapour is at the temperature greater than the saturation temperature, it is said to exist at superheated state. Gases are highly superheated vapour.

Change of Phase (at different pressures)

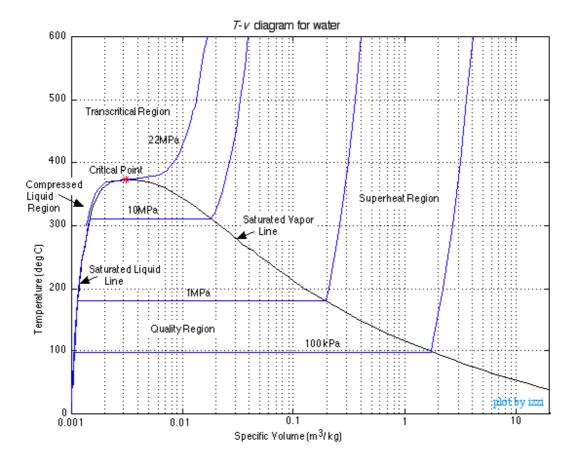
Consider unit mass of ice below freezing point, enclosed in a piston-cylinder assembly. Heat is transferred to the system under different pressures.

AT A LOWER PRESSURE (<1 atm.)

- > Slight rise in melting point.
- Marked drop in boiling point.
- Marked increase in the change of volume which accompanies evaporation.
- When the pressure is reduced to 0.006112 bar, the melting and boiling temperatures become equal (273.16 K) and the change of phase, ice-water-steam is represented by a single horizontal line. At this state, ice, water and steam co-exist in thermodynamic equilibrium in a closed vessel, and it is called **triple point line**.
- If the pressure is reduced still further, the ice, instead of melting, sublimates directly into steam.

AT A HIGHER PRESSURE (> 1 atm.)

- Marked reduction in the change of volume accompanying evaporation.
- ➤ At a sufficiently high pressure, the change of volume falls to zero and the horizontal portion of the curve reduces to a point of inflexion. This is referred to as the critical point.

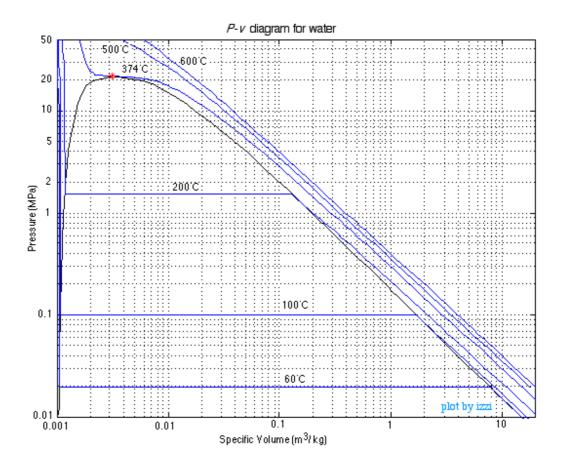


Critical Pressure, $P_c = 221.2$ bar

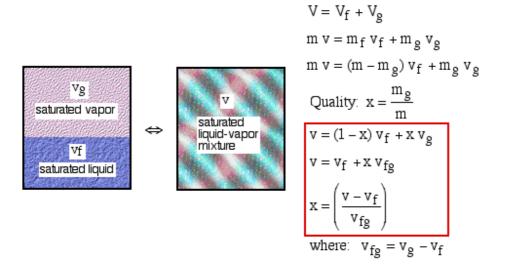
Critical Temperature, $T_c = 647.3 \text{ K}$

Critical Volume, $T_v = 0.00317 \text{ m}^3/\text{kg}$

➤ At pressure above critical, there is no definite transition from liquid to vapour.



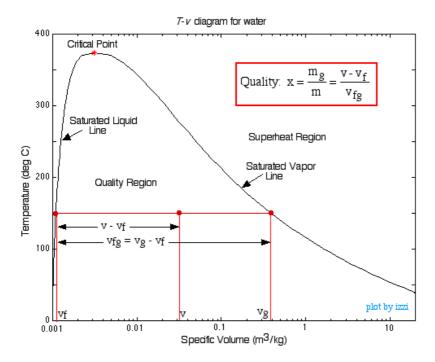
Properties of Two Phase Mixture



 $v = v_l + x.v_{lg}$ (specific volume)

 $h = h_l + x.h_{lg}$ (specific enthalpy)

 $s = s_l + x.s_{lg}$ (specific entropy)



Other Thermodynamic Properties

Internal Energy

The molecular internal energy or simple internal energy is the sum of all the microscopic forms of energy of a system. The **microscopic energy mode** refers to the energy stored in the molecular and atomic structure of the system.

If E represents the energy of one molecule,

$$E = E_{trans} + E_{rot} + E_{vib} + E_{chem} + E_{electronic} + E_{nuclear}$$

If N is the total number of molecules in the system, then the total internal energy

$$U = NE$$

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

$$U = f(T)$$
 only

Enthalpy

Enthalpy is the algebraic sum of internal energy and flow energy (pressure energy). Mathematically,

$$H = U + PV$$

It is a thermodynamic property.

$$\begin{aligned} H_2 - H_1 &= U_2 - U_1 + P_2 V_2 - P_1 V_1 \\ &= m C_v (T_2 - T_1) + m R (T_2 - T_1) \\ &= (T_2 - T_1) m (C_v + R) \end{aligned}$$
 Hence, $H_2 - H_1 = m C_p (T_2 - T_1)$

The concept of enthalpy has emerged to describe a control mass undergoing a quasi-equilibrium constant pressure process. Further, we assume no changes in kinetic and potential energy and the only work done during the process is in terms of boundary movement.

$$Q_{12} = U_2 - U_1 + W_{1-2}$$

$$= U_2 - U_1 + P(V_2 - V_1)$$

$$Q_{12} = (U_2 + PV_2) - (U_1 + PV_1)$$

$$= H_2 - H_1$$

Specific Heats

Specific heat is defined as the amount of heat required per unit mass to raise the temperature of a substance by one degree.

$$C = \frac{\delta q}{dT}$$

Unit: kJ / kg.K

$$\delta Q = dU + \delta W = dU + P.dV$$

This expression can be evaluated for two separate special cases:

1. Constant Volume, for which the work term (P.dV) is zero, so that the specific heat (at constant volume) is:

$$Cv = \frac{1}{m} \left(\frac{\delta Q}{\delta T} \right) at \ constant \ volume$$

$$= \frac{1}{m} \left(\frac{\partial U}{\partial T} \right) at \ constant \ volume$$

$$= \left(\frac{\partial u}{\partial T} \right) at \ constant \ volume$$

2. Constant Pressure, for which the work term can be integrated and the resulting PV term at the initial and final states be associated with internal energy terms:

$$Cv = \frac{1}{m} \left(\frac{\delta Q}{\delta T} \right)$$
 at constant pressure
$$= \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)$$
 at constant pressure
$$= \left(\frac{\partial h}{\partial T} \right)$$
 at constant pressure

Also,

$$\bullet \quad C_p - C_v = R$$

•
$$Cv = \frac{R}{\gamma - 1}$$

•
$$Cp = \frac{\gamma R}{\gamma - 1}$$

CHAPTER 3

PROPERTIES OF COMMON SUBSTANCE

3.1 Pure Substance and State Postulate

Pure implies substances composed of a single chemical species. Hence a pure substance is a system which is

- (a) homogeneous in chemical composition,
- (b) homogeneous in chemical aggregation, and
- (c) invariable in chemical composition.

Homogeneous in chemical composition means that the composition of each part of the system is the same as the compositions of every other part. Composition means relative proportion of the chemical elements into which the sample can be analyzed. It does not matter how these elements are combine.

In Figure 3.1 for example, system (i), comprising steam and water, is homogeneous in composition, since chemical analysis would reveal that hydrogen and oxygen atoms are present in the ratio 2:1 whether the sample be taken from the steam or from the water. The same is true for system (ii), containing uncombined hydrogen and oxygen gas in the atomic ratio 2:1 in the upper part, and water in the lower part. System (iii) however is not homogeneous in composition; for the hydrogen and oxygen are present in the ratio 1:1 in the upper part, but in the ratio 2:1 (as water) in the lower part.

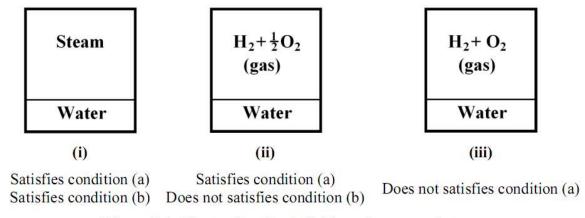


Figure 3.1: Illustrating the definition of a pure substance

Homogeneous in chemical compostion means that the chemical elements must be combined chemically in the same way in all parts of the system. Consideration of Figure 3.1 shows that system (i) satisfies this condition also; for steam and water consists of identical molecules. System (ii) on the other hand is not homogeneous in chemical aggregation since, in the upper part of the system, the hydrogen and oxygen are not combined chemically (individual atoms of H and O are not uniquely associated), whereas in the lower part of the system the he hydrogen and oxygen are combined in the form of water.

Invariable chemical aggregation means that the state of the chemical combination of the system does not change with time. Thus a mixture of hydrogen and oxygen, which changed into steam during the time that the system was under consideration, would not be a pure substance.

The important characteristic of a pure substance is that it is invariable in chemical composition even though there may be a change of phase. Thus, a system consisting of a mixture of various phases of water viz. water and ice, water and steam is a pure substance. Similarly, a system consisting of oxygen as a vapor; a liquid or a combination of these is also a pure substance. Air, however, though a mixture of several gases is considered as a pure substance only as long as it is all gas or all liquid. A mixture of dry gaseous air and liquid air is not a pure substance, because chemical composition of liquid phase is different from that of vapor phase.

State Postulates

The number of properties required to fix the state of a system is given by the state postulate and is defined as the general rule that is developed as a guide in determining the number of independent properties required to fix the state of a system.

For a pure simple compressible substance, repeated observations and experiments show that two independent properties are necessary and sufficient to establish the stable equilibrium state of a system. The word simple and compressible imply that the only work mode considered is the PdV work form. A system is called a simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.

The observed behavior of a pure simple compressible substance is summarized in the state postulates:

The values of any two independent thermodynamic properties are sufficient to establish the stable thermodynamic state of a pure simple compressible substance.

If T and v are known for a pure compressible substance, then P and u have unique known values. Mathematically this is given as

P=P(T,v) and u=u(T,v)

3.2 Ideal Gas

A perfect gas or an ideal gas is defined as a gas having no forces of molecular attraction. A gas which follows the gas laws at all ranges of pressures and temperatures can be considered as an ideal gas but no such gas exists in nature. However, real gases tend to follow these laws at low pressures or high temperatures or at both. This is because the molecules are far apart at reduced pressures and elevated temperatures and the force of attraction between them tends to be small. At low pressures, the gases behave nearly as ideal gases. The range of this low pressure is different for different gases.

3.2.1 Boyle's Law

This law was enunciated by Robert Boyle in 1661 on the basis of his experimental results. Boyle's law may be stated as follows:

If the temperature remains constant, the volume of a given mass of gas is inversely proportional to the pressure.

$$V \propto \left(\frac{1}{p}\right)_T$$

3.2.2 Charles' Law

This law, also known as Gay-Lussac's law, was enunciated in 1787. It may be stated in parts:

(a) If the pressure is held constant, the volume of a given mass of gas varies directly as the absolute temperature.

$$V \propto (T)_P$$

(b) If the volume is held constant, the pressure of a given mass of gas varies directly as the absolute temperature.

$$P \propto (T)_V$$

A relation between all the three variables P, V and T may be obtained by combining Boyle's law and Charles' law. Referring to Figure 3.2, consider unit mass of a gas in state 1 and let it undergo an arbitrary change to state 2. From state 1, draw a constant pressure line, and from

state 2 draw a constant temperature line. The two lines intersect at point A.

Now applying Charle's law for the process 1-A

$$\frac{V_1}{V_A} = \frac{T_1}{T_A}$$

$$V_A = \frac{T_A}{T_1} V_1 = \frac{T_2}{T_1} V_1$$
 (i)

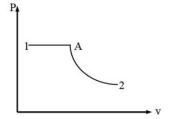


Figure 3.2: Relation between P, v, and T

Applying Boyle's law for the process A-2

$$\frac{V_2}{V_A} = \frac{P_A}{P_2}$$

$$V_A = \frac{P_2}{P_A} V_1 = \frac{P_2}{P_1} V_1$$
 (ii)

Combining equation (i) and (ii)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{PV}{T} = R$$

where R is a constant for a given gas. The constant is called the characteristic gas constant and has the units of J/kg.K or m-kgf/kg.K.

For a system consisting of a mass of kg of gas,

PV=mRT

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FIGURE 3-6

At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).



FIGURE 3-7

At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

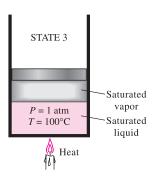


FIGURE 3-8

As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture*).

important phase-change process, attention in this section is focused on the liquid and vapor phases and their mixture. As a familiar substance, water is used to demonstrate the basic principles involved. Remember, however, that all pure substances exhibit the same general behavior.

Compressed Liquid and Saturated Liquid

Consider a piston–cylinder device containing liquid water at 20°C and 1 atm pressure (state 1, Fig. 3–6). Under these conditions, water exists in the liquid phase, and it is called a **compressed liquid**, or a **subcooled liquid**, meaning that it is *not about to vaporize*. Heat is now transferred to the water until its temperature rises to, say, 40°C. 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 cylinder remains constant at 1 atm during this process since it depends on the outside barometric pressure and the weight of the piston, both of which are constant. Water is still a compressed liquid at this state since it has not started to vaporize.

As more heat is transferred, the temperature keeps rising until it reaches 100°C (state 2, Fig. 3–7). 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 take place. A liquid that is *about to vaporize* is called a **saturated liquid**. Therefore, state 2 is a saturated liquid state.

Saturated Vapor and Superheated Vapor

Once boiling starts, the temperature stops rising until the liquid is completely vaporized. That is, the temperature will remain constant during the entire phase-change process if the pressure is held constant. This can easily be verified by placing a thermometer into boiling pure water on top of a stove. At sea level (P=1 atm), the thermometer will always read 100° C if the pan is uncovered or covered with a light lid. During a boiling process, the only change we will observe is a large increase in the volume and a steady decline in the liquid level as a result of more liquid turning to vapor.

Midway about the vaporization line (state 3, Fig. 3–8), the cylinder contains equal amounts of liquid and vapor. As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized (state 4, Fig. 3–9). At this point, the entire cylinder is filled with vapor that is on the borderline of the liquid phase. 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 a **saturated vapor**. 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 the *liquid and vapor phases coexist* in equilibrium at these states.

Once the phase-change process is completed, we are back to a single-phase region again (this time vapor), and further transfer of heat results in an increase in both the temperature and the specific volume (Fig. 3–10). At state 5, the temperature of the vapor is, let us say, 300°C; and if we transfer some heat from the vapor, the temperature may drop somewhat but no condensation will take place as long as the temperature remains above 100°C

(for P = 1 atm). A vapor that is *not about to condense* (i.e., not a saturated vapor) is called a **superheated vapor**. Therefore, water at state 5 is a superheated vapor. This constant-pressure phase-change process is illustrated on a T-V diagram in Fig. 3–11.

If the entire process described here is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during the heating process.

In our daily life, water implies liquid water and steam implies water vapor. In thermodynamics, however, both water and steam usually mean only one thing: H₂O.

Saturation Temperature and Saturation Pressure

It probably came as no surprise to you that water started to boil at 100°C. Strictly speaking, the statement "water boils at 100°C" is incorrect. The correct statement is "water boils at 100°C at 1 atm pressure." The only reason water started boiling at 100°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°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** $T_{\rm sat}$. Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the **saturation pressure** $P_{\rm sat}$. At a pressure of 101.325 kPa, $T_{\rm sat}$ is 99.97°C. Conversely, at a temperature of 99.97°C, $P_{\rm sat}$ is 101.325 kPa. (At 100.00°C, $P_{\rm sat}$ is 101.42 kPa in the ITS-90 discussed in Chap. 1.)

Saturation tables that list the saturation pressure against the temperature (or the saturation temperature against the pressure) are available for

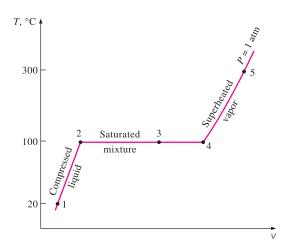


FIGURE 3-11

T-V diagram for the heating process of water at constant pressure.



FIGURE 3-9

At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).



FIGURE 3-10

As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

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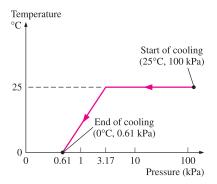


FIGURE 3-14

The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from 25°C to 0°C.

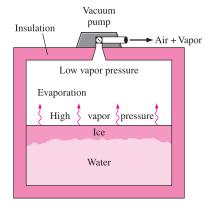


FIGURE 3-15

In 1775, ice was made by evacuating the air space in a water tank.



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from the products to be cooled. The heat of vaporization during evaporation is absorbed from the products, which lowers the product temperature. The saturation pressure of water at 0°C is 0.61 kPa, and the products can be cooled to 0°C by lowering the pressure to this level. The cooling rate can be increased by lowering the pressure below 0.61 kPa, but this is not desirable because of the danger of freezing and the added cost.

In vacuum cooling, there are two distinct stages. In the first stage, the products at ambient temperature, say at 25°C, are loaded into the chamber, and the operation begins. The temperature in the chamber remains constant until the *saturation pressure* is reached, which is 3.17 kPa at 25°C. In the second stage that follows, saturation conditions are maintained inside at progressively *lower pressures* and the corresponding *lower temperatures* until the desired temperature is reached (Fig. 3–14).

Vacuum cooling is usually more expensive than the conventional refrigerated cooling, and its use is limited to applications that result in much faster cooling. Products with large surface area per unit mass and a high tendency to release moisture such as lettuce and spinach are well-suited for vacuum cooling. Products with low surface area to mass ratio are not suitable, especially those that have relatively impervious peels such as tomatoes and cucumbers. Some products such as mushrooms and green peas can be vacuum cooled successfully by wetting them first.

The vacuum cooling just described becomes **vacuum freezing** if the vapor pressure in the vacuum chamber is dropped below 0.61 kPa, the saturation pressure of water at 0°C. The idea of making ice by using a vacuum pump is nothing new. Dr. William Cullen actually made ice in Scotland in 1775 by evacuating the air in a water tank (Fig. 3–15).

Package icing is commonly used in small-scale cooling applications to remove heat and keep the products cool during transit by taking advantage of the large latent heat of fusion of water, but its use is limited to products that are not harmed by contact with ice. Also, ice provides *moisture* as well as *refrigeration*.

3-4 PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

The variations of properties during phase-change processes are best studied and understood with the help of property diagrams. Next, we develop and discuss the T-V, P-V, and P-T diagrams for pure substances.

1 The T-v Diagram

The phase-change process of water at 1 atm pressure was described in detail in the last section and plotted on a T- ν diagram in Fig. 3–11. Now we repeat this process at different pressures to develop the T- ν diagram.

Let us add weights on top of the piston until the pressure inside the cylinder reaches 1 MPa. 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. 3–16, but there are some noticeable differences. First, water starts boiling at a much higher tempera-

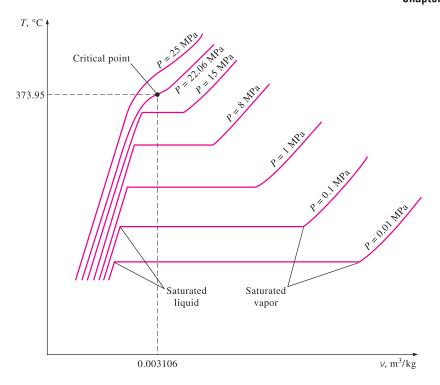


FIGURE 3-16

T-v diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

ture (179.9°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. 3–16, and it becomes a point when the pressure reaches 22.06 MPa 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* $T_{\rm cr}$, *critical pressure* $P_{\rm cr}$, and *critical specific volume* $v_{\rm cr}$. The critical-point properties of water are $P_{\rm cr}=22.06$ MPa, $T_{\rm cr}=373.95$ °C, and $v_{\rm cr}=0.003106$ m³/kg. For helium, they are 0.23 MPa, -267.85°C, and 0.01444 m³/kg. The critical properties for various substances are given in Table A–1 in the appendix.

At pressures above the critical pressure, there is not a distinct phase-change process (Fig. 3–17). 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

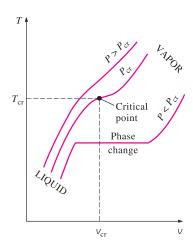


FIGURE 3–17

At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

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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.

The saturated liquid states in Fig. 3–16 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. 3–18. 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**.

2 The P-v Diagram

The general shape of the P- ν diagram of a pure substance is very much like the T- ν diagram, but the T = constant lines on this diagram have a downward trend, as shown in Fig. 3–19.

Consider again a piston-cylinder device that contains liquid water at 1 MPa and 150°C. Water at this state exists as a compressed liquid. Now the weights on top of the piston are removed one by one so that the pressure inside the cylinder decreases gradually (Fig. 3–20). The water is allowed to exchange heat with the surroundings so its temperature remains constant. As

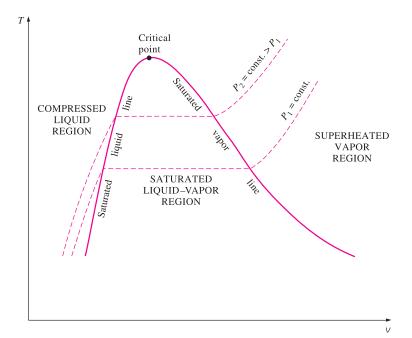


FIGURE 3–18 T- ν diagram of a pure substance.

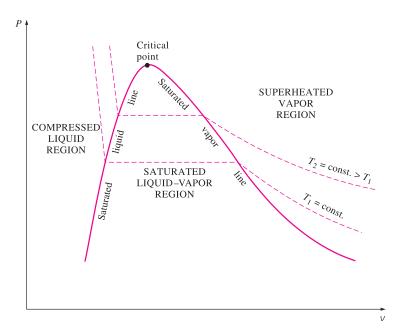


FIGURE 3–19 P-V diagram of a pure substance.

the pressure decreases, the volume of the water increases slightly. When the pressure reaches the saturation-pressure value at the specified temperature (0.4762 MPa), the water starts to boil. During this vaporization process, both the temperature and the pressure remain constant, but the specific volume increases. Once the last drop of liquid is vaporized, further reduction in pressure results in a further increase in specific volume. Notice that during the phase-change process, we did not remove any weights. Doing so would cause the pressure and therefore the temperature to drop [since $T_{\rm sat} = f(P_{\rm sat})$], and the process would no longer be isothermal.

When the process is repeated for other temperatures, similar paths are obtained for the phase-change processes. Connecting the saturated liquid and the saturated vapor states by a curve, we obtain the P- ν diagram of a pure substance, as shown in Fig. 3–19.

Extending the Diagrams to Include the Solid Phase

The two equilibrium diagrams developed so far represent the equilibrium states involving the liquid and the vapor phases only. However, these diagrams can easily be extended to include the solid phase as well as the solid–liquid and the solid–vapor saturation regions. The basic principles discussed in conjunction with the liquid–vapor phase-change process apply equally to the solid–liquid and solid–vapor phase-change processes. Most substances contract during a solidification (i.e., freezing) process. Others, like water, expand as they freeze. The $P-\nu$ diagrams for both groups of substances are given in Figs. 3–21 and 3–22. These two diagrams differ only in



FIGURE 3-20

The pressure in a piston—cylinder device can be reduced by reducing the weight of the piston.

3.4 Property of a Two phase Mixture/Quality

During a vaporization process, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor(Fig. 3–34). To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture. This is done by defining a new property called the *quality* x as the ratio of the mass of vapor to the total mass of the mixture:

$$x = \frac{m_{vapor}}{m_{total}} = \frac{m_g}{m}$$

where,
$$m_{total} = m_{liquid} + m_{vapor} = m_l + m_g$$

Quality has significance for saturated mixtures only. It has no meaning in the compressed liquid or superheated vapor regions. Its value is between 0 and 1. The quality of a system that consists of saturated liquid is 0 (or 0 percent), and the quality of a system consisting of saturated vapor is 1 (or 100 percent).

Consider a tank that contains a saturated liquid–vapor mixture. The volume occupied by saturated liquid is V_l , and the volume occupied by saturated vapor is V_g . The total volume V is the sum of the two:

$$V = V_l + V_g$$

$$mv = m_l v_l + m_g v_g$$

$$v = \frac{m_l}{m} v_l + \frac{m_g}{m} v_g$$

$$v = (1 - x) v_l + x v_g$$

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

$$v = v_l + x v_{lg}$$

Critical point

Saturated Saturated vapor Vapor $v < v_f$ $v_f < v < v_g$ Specific volume

Specific volume

where, v_{lg} is defined as the difference between the specific volumes of the saturated vapor and the saturated liquid i.e. $v_{lg} = (v_g - v_l)$.

Any intensive property such as h,u,s can be evaluated for a state in the saturated/wet region by relating it with quality (x) i.e. for any intensive property 'z', we can write,

$$z = z_l + x z_{lg}$$

i.e.

$$u = u_l + x u_{la}$$

$$h = h_l + x h_{lg}$$

3.5 Other Thermodynamic Properties

3.5.1. Enthalpy: A combine property

In the analysis of certain types of processes, particularly in power generation and refrigeration, we frequently encounter the combination of properties u+PV. For the sake of simplicity and convenience, this combination is defined as a new property, enthalpy, and denoted by 'h'

h=u+Pv(kJ/kg)

H=U+PV (kJ)

3.5.2 Specific Heat

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree. In thermodynamics, we are interested in two kinds of specific heats: specific heat at constant volume c_v and specific heat at constant pressure c_p .

Physically, the specific heat at constant volume c_{ν} can be viewed as the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant. The energy required to

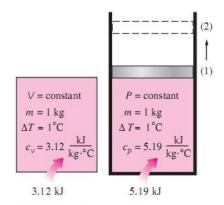


FIGURE 4-19

Constant-volume and constantpressure specific heats c_v and c_p (values given are for helium gas).

do the same as the pressure is maintained constant is the specific heat at constant pressure c_p . The specific heat at constant pressure c_p is always greater than c_v because at constant pressure the system is allowed to expand and the energy for this expansion work must also be supplied to the system.

In thermodynamics, specific heat at constant volume c_v is defined as the change in the internal energy of a substance per unit change in temperature at constant volume.

$$c_{V} = \left(\frac{\partial u}{\partial T}\right)_{V}$$

Likewise, specific heat at constant pressure c_p can be defined as the change in the enthalpy of a substance per unit change in temperature at constant pressure.

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

In other words, c_{ν} is a measure of the variation of internal energy of a substance with temperature, and c_{p} is a measure of the variation of enthalpy of a substance with

temperature. Thus, change in internal energy and enthalpy can be written as:

$$du = c_{\nu}(T) dT$$

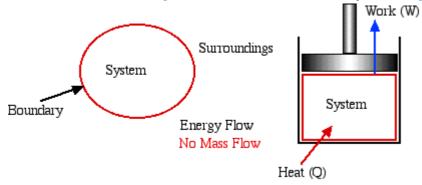
$$dh = c_n(T) dT$$

First Law of Thermodynamics

"Energy can neither be created nor destroyed but it can be transformed from one form to another."

"If something enters into the system, it comes out in any other form but does not vanish."

First Law of Thermodynamics for Control Mass (Closed System/Non Flow Process)



Let us consider a closed system with heat input and work output as shown in figure.

Using Conservation of Energy Equation,

[Energy entering into the system] – [Energy leaving the system] =

[Change in total energy of the system]

or,
$$E_{in} - E_{out} = \Delta E_s$$

$$\Rightarrow$$
 Q - W = ΔE_{cm} (i)

Where, total energy of control mass (ΔE_{cm}) is algebraic sum of Kinetic Energy (K.E.), Potential Energy (P.E.) and Internal Energy of the system.

Mathematically,

$$E_{cm} = K.E. + P.E. + U$$

$$\Rightarrow \Delta E_{cm} = \Delta K.E. + \Delta P.E. + \Delta U$$

In a closed system, change in K.E. and change in P.E. are negligible as compared to change in U of the system.

Therefore, $\Delta E_{cm} = \Delta U$

So, from equation (i), we get,

$$Q - W = \Delta U$$

Therefore,
$$\delta Q - \delta W = dU$$

Case I: If a closed system undergoes cyclic process

Conservation of Energy Equation can be written as:

$$\oint (\delta Q - \delta W) = \oint dU$$

Internal Energy is a property of thermodynamic system. From the definition of property, $\oint dU = 0$

Hence, Conservation of Energy Equation for a cyclic process becomes

$$\oint (\delta Q - \delta W) = 0$$

or,
$$\oint \delta Q = \oint \delta W$$

Hence,
$$Q_{net} = W_{net}$$

Hence, the first law of thermodynamics for a cycle states that:

"During any cycle a system (control mass) undergoes, the cyclic integral of the heat is proportional to the cyclic integral of work."

Case II: For any thermodynamic process 1-2,

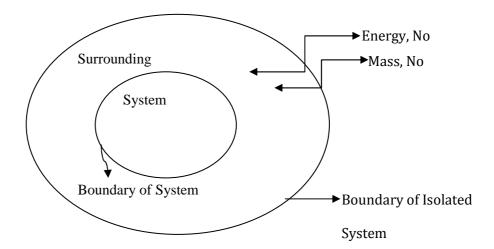
In a closed system, the conservation of energy equation becomes

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

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

Conservation of Energy Equation for Isolated System (Universe)

Let us consider an isolated system as shown in figure below.



Using Conservation of Energy Equation,

[Energy entering into the system] – [Energy leaving the system] =

[Change in total energy of the system]

or,
$$E_{in} - E_{out} = \Delta E_s$$

or,
$$0 - 0 = \Delta ES$$

or,
$$\Delta E_s = 0$$

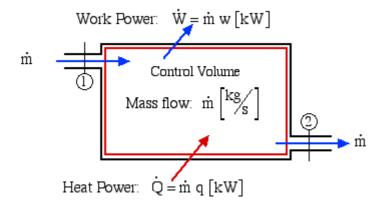
Integrating both sides,

$$\int dEs = \int 0$$

Hence,
$$E_s = 0$$

Hence, total energy of isolated system (universe) is always constant.

Conservation of Energy Equation for Control Volume (Open System/Flow Process)



Let us consider an open system with single inlet (1) and outlet (2) as shown in figure. The following quantities are defined with reference to the figure.

 $m_1, m_2 \rightarrow mass flow rate, kg/s$

 $P_1, P_2 \rightarrow pressure$ (absolute), N/m₂

 $v_1, v_2 \rightarrow \text{specific volume, m}^3/\text{kg}$

u1, u2 \rightarrow specific internal energy, J/kg

 $V_1, V_2 \rightarrow \text{velocity, m/s}$

 $z_1, z_2 \rightarrow$ elevation above an arbitrary datum, m

The total power in due to heat and mass flow through the inlet port (1) must equal the total power out due to work and mass flow through the outlet port (2), thus:

$$\dot{Q} + \dot{m} e_1 = \dot{W} + \dot{m} e_2$$

$$\dot{Q} - \dot{W} = \dot{m} (e_2 - e_1) = \dot{m} \Delta e$$

Since there is no accumulation of energy(steady flow), the total rate of flow of all energy streams entering the control volume must equal to the total rate of flow of all the energy streams leaving the C.V. So,

Change in flow rate of energy = 0

Hence, energy flow rate into the system = energy flow rate out of the system

Also, Mass flow rate into the system = Mass flow rate out of the system

The specific energy e can include kinetic and potential energy however will always include the combination of internal energy (u) and flow work (PV), thus we conveniently combine these properties in terms of the property enthalpy, as follows:

$$e = \underbrace{u + P v}_{h} + ke + pe = h + \begin{bmatrix} V^{2} \\ 2 \end{bmatrix} + g z$$

$$h \Rightarrow \text{enthalpy}$$

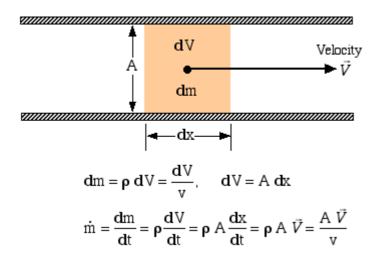
Note that z is the height of the port above some datum level [m] and g is the acceleration due to gravity [9.81 m/s2]. Substituting for energy e in the above energy equation and simplifying, we obtain the final form of the energy equation for a single-inlet single-outlet steady flow control volume as follows:

$$\dot{Q} - \dot{W} = \dot{m} \left[\Delta h + \left(\Delta V^2 \right) + g \Delta z \right]$$

Notice that enthalpy h is fundamental to the energy equation for a control volume. The above is a Steady State Steady Flow (SSSF) Energy Equation.

Mass Balance

Consider an elemental mass dm flowing through an inlet or outlet port of a control volume, having an area A, volume dV, length dx, and an average steady velocity \vec{V} , as follows.



Thus finally the mass flow rate $\dot{\mathbf{m}}$ can be determined as follows:

$$\begin{split} \dot{m} &= \rho \ \dot{V} = \frac{\dot{V}}{v} = \rho \ A \ \vec{V} = \frac{A \ \vec{V}}{v} \\ \text{where: } \dot{m} \text{ is the mass flow rate } \begin{bmatrix} kg \\ s \end{bmatrix} \\ \dot{V} \text{ is the volumetric flow rate } \begin{bmatrix} m^3 \\ s \end{bmatrix} \\ \rho \text{ is the density } \begin{bmatrix} kg \\ m^3 \end{bmatrix}, \text{ } v \text{ is the specific volume } \begin{bmatrix} m^3 \\ kg \end{bmatrix} \\ \vec{V} \text{ is the velocity } \begin{bmatrix} m \\ s \end{bmatrix} \text{ } A \text{ is the flow area } \begin{bmatrix} m^2 \end{bmatrix} \end{split}$$

Steady State Work Applications	Steady State Flow Applications
Pump, Turbine, Fan, Compressor	Boiler, Nozzle, Heat exchanger, Diffuser, Pipe,
	Expansion valve/Throttling valve

Analysis of Control Volume at Steady State, Steady Flow Process

The SSSF energy equation for C.V. does not include the short-term transient start up or shut down of the devices but only the steady operating period of time.

- 1. The control volume is fixed i.e. it does not move relative to the co-ordinate frame. It implies that there is no work associated with the acceleration of the control volume.
- 2. The state of the mass at each point of the C.V. does not vary with time i.e. a steady state. To fulfill this assumption, we follow the conditions:

$$\frac{d(mcv)}{dt} = 0$$
 and $\frac{d(Ecv)}{dt} = 0$

3. The mass that flows across the control surface i.e. mass flux and the state of this mass at each discrete area of flow on the control surface do not vary with time i.e. a steady flow. The rate of energy transfer by heat and work throughout the control surface remain constant,

Conditions for SSSF Work and Flow Devices

For all flow devices, W = 0

For all work devices, $W \neq 0$

Pump, compressor, fan \rightarrow -ve work

Turbine \rightarrow +ve work

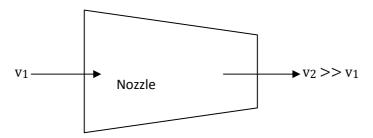
Assumptions for SSSF Work and Flow Devices

- 1. Except boiler and heat exchanger, all work and flow devices can be taken as adiabatic. (Q=0)
- 2. For all work and flow devices, change in P.E. can be neglected.
- 3. Except nozzle and diffuser, change in K.E. can be neglected in all work and flow devices.
- 4. In case of nozzle, inlet velocity can be neglected in comparison to outlet velocity.

In case of diffuser, exit velocity can be neglected in comparison to inlet velocity.

Examples of SSSF Processes

1. Nozzle and Diffuser



A nozzle is a SSSF device having a flow-passage of varying cross-section area in which the velocity of fluid increases in the direction of flow with a corresponding drop in pressure.

a. Nozzle is flow device. So, W = 0Hence, SSSF energy equation reduces to

$$\dot{Q} = \dot{m} \left[\Delta h + \left(\Delta V^2 / 2 \right) + g \Delta z \right]$$
(i)

b. For an adiabatic process Q = 0. Hence, equation (i) reduces to

$$0 = \dot{m} \left[\Delta h + \left(\frac{\Delta V^2}{2} \right) + g \Delta z \right]$$

$$0 = \Delta h + \left(\Delta V^2 / 2\right) + g \Delta z$$
.....(ii)

c. In case of horizontal nozzle, $z_1 = z_2$.

Hence, equation (ii) becomes

$$0 = \Delta h + \left(\Delta V^2 / 2\right) \qquad(iii)$$

d. If inlet velocity of nozzle is negligible in comparison to exit velocity, equation (iii) reduces to:

$$(h_2 - h_1) + (v_2)^2/2 = 0$$

A diffuser is a SSSF device in which the high velocity fluid decelerates in the direction of flow with a corresponding increase in pressure.

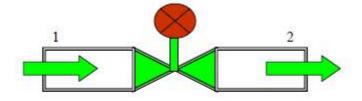
Since,
$$v_2 \ll v_1$$

Hence,
$$(h_2 - h_1) + (v_1)^2/2 = 0$$

2. Throttling Valve

When a fluid flows through a constricted passage, like a partially opened valve, an orifice or a porous plug, there is an appreciable drop in pressure, and the flow is said to be throttled.

Consider the flow of fluid through a small valve as shown



if the SFEE is applied between sections 1 and 2:

$$Q - W = m (\Delta h + \Delta ke + \Delta Pe)$$

Q = 0 Assuming adiabatic

W = 0 No displacement work (no work is inputted or extracted, ie no pump or turbineis attached)

 $\Delta ke = 0$ Assumed (inlet and exit velocities are similar or slow)

 $\Delta Pe = 0$ Assumed (entry and exit at the same or nearly the same elevation)

Hence, The SFEE, reduces to:

$$m(h2-h1)=0$$

divide by the mass flow m to get:

$$h2 = h1$$

hence for a control valve, the enthalpy of the fluid remains constant.

3. Turbine and Compressor

Turbine is a SSSF device that produces work due to the pressure drop of the working fluid when the fluid passes through a set of blades attached to a shaft free to rotate.

For a turbine,
$$\frac{W}{m} = \Delta h$$

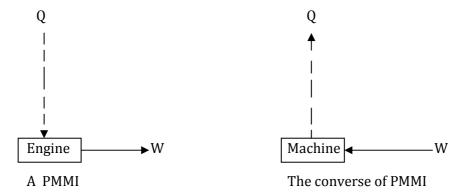
Where,
$$\Delta h = h_1 - h_2$$
 since $h_2 < h_1$ (for turbine), $W = +ve$

For a pump or compressor,
$$rac{W}{m}=\Delta h$$

Where,
$$h = h_2 - h_1$$
 since $h_2 > h_1$ (for turbine), $W = -ve$

Perpetual Motion Machine of the First Kind - PMMI

PMMI violates First Law of Thermodynamics (Conservation of Energy).



There can be no machine which could continuously supply mechanical work without some other form of energy disappearing simultaneously. Such a fictitious machine is called PMMI.

The converse of the above statement is also true.

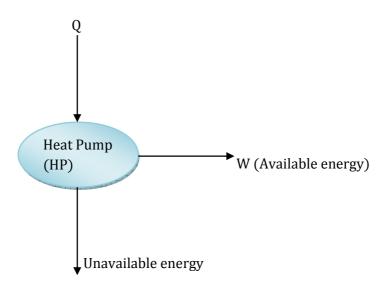
Second Law of Thermodynamics

Necessity of Formulation of Second Law

- The first law of thermodynamics states that a certain energy balance will hold when a system undergoes a change of state or a thermodynamic process. But ut does not give any information on whether the change of state or the process is at all feasible or not.
- The Second Law gives directional possibility of physical phenomena and concept of entropy.

Entropy

Entropy is the randomness or disorder of a thermodynamics system. It is an extensive property of a system that is used to measure unavailable energy (loss).



Increase in entropy

- ⇒ Increase in randomness
- ⇒ Increase in unavailable energy
- ⇒ Decrease in available energy

Mathematically, change in entropy can be written as

$$dS \ge \frac{\delta Q}{T}$$
 > - Irreversible Process (......)
= - Reversible Process (_____)

Entropy Balance Equation can be written as:

[Entropy entering into the system] – [Entropy leaving the system]

+ [Entropy generation of the system] = [Change in entropy of the system]

Hence,
$$S_{in} - S_{out} + S_{gen} = \Delta S$$

Isolated System

$$S_{gen} = \Delta S$$

Closed System

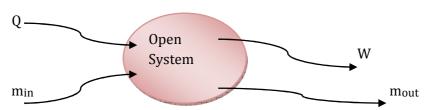


$$\sum_{T} \frac{Q}{T}(entering) - 0 + S(generated) = \Delta S(control mass)$$

[Since, Work is entropy free energy. So, $S_{out} = 0$]

Hence, $\sum_{T}^{Q}(entering) + S(generated) = \Delta S(control mass)$

Open System



$$\sum \frac{Q}{T} (entering) + m.s (in) - m.s (out) + S(generated) = \Delta S(control volume)$$

Differentiating both sides w.r.t. time,

$$\sum \frac{\dot{Q}}{T} (entering) + \dot{m}.s (in) - \dot{m}.s (out) + \dot{S}(generated) = \Delta \dot{S}(control \ volume)$$

This is the Second Law for Unsteady Flow.

For SSSF,

$$\Delta S$$
 (control volume) = 0

$$m_{in} = m_{out} = m$$
 (say) Then,

$$\sum_{T} \frac{\dot{Q}}{T} (entering) + \dot{m}[s(in) - s(out)] + \dot{S}(generated) = 0$$

Reversible and Irreversible Processes

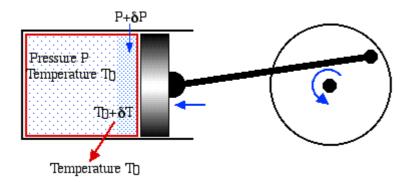
Reversible Process

A process is reversible if, after the process has been completed, means can be found to restore the system and all elements of its surroundings to their respective initial states.

Irreversible Process

A process is called irreversible if the system and all parts of the surroundings cannot be exactly restored to their respective initial states after the process has occurred.

Consider an example of a reversible piston cylinder device in thermal equilibrium with the surroundings at temperature T₀, and undergoing a cyclic compression/expansion process.



For mechanical reversibility we assume that the process is frictionless, however we also require that the process is a quasi-equilibrium one. In the diagram we notice that during compression the gas particles closest to the piston will be at a higher pressure than those farther away, thus the piston will be doing more compression work than it would do if we had waited for equilibrium conditions to occur after each incremental step. Similarly, thermal reversibility requires that all heat transfer is isothermal. Thus if there is an incremental rise in temperature due to compression then we need to wait until thermal equilibrium is established. During expansion the incremental fall in temperature will result in heat being transferred *from* the surroundings *to* the system until equilibrium is established.

In summary, there are three conditions required for reversible operation:

- All mechanical processes are frictionless.
- At each incremental step in the process thermal and pressure equilibrium conditions are established.
- All heat transfer processes are isothermal.

Change in Entropy for Ideal Gas/Perfect Gas/Compressible Substance

Using First Law of Thermodynamics

From definition of entropy for reversible process,

From (i) and (ii), $T. dS - \delta W = dU$

Or,
$$T. dS = \delta W + dU$$

Or,
$$T.dS = P.dV + dU \dots (iii)$$

From definition of enthalpy,

$$H = U + PV$$

Differentiating both sides,

$$dH = dU + p. dV + V. dP$$

Or,
$$dH = T \cdot dS + V \cdot dP$$

$$Or, T. dS = dH - V. dP (iv)$$

From equation (iii),

$$dS = \frac{dU}{T} + \frac{P.dV}{T}$$

Or,
$$dS = \frac{m.Cv.dT}{T} + m.R.\frac{dV}{V}$$
 [Since, $PV = mRT$]

Integrating both sides,

$$\int_{S1}^{S2} dS = \int_{T1}^{T2} m. Cv. \frac{dT}{T} + \int_{V1}^{V2} m. R. \frac{dV}{V}$$

$$\Rightarrow S_2 - S_1 = m \int_{T_1}^{T_2} Cv \cdot \frac{dT}{T} + mR \log_e \frac{v_2}{v_1}$$

This equation is for variable specific heat capacity.

$$\Rightarrow S_2 - S_1 = m. Cv. \log_e \frac{T^2}{T^1} + mR \log_e \frac{V^2}{V^1}$$

From equation (iv),

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

$$\Rightarrow dS = \frac{m.Cp.dT}{T} - m.R.\frac{dP}{P}$$

Integrating both sides,

$$\int_{S1}^{S2} dS = \int_{T1}^{T2} m. Cp. \frac{dT}{T} - \int_{P1}^{P2} m. R. \frac{dP}{P}$$

$$\Rightarrow S_2 - S_1 = m \int_{T_1}^{T_2} Cp \cdot \frac{dT}{T} - mR \log_e \frac{P_2}{P_1}$$

This equation is for variable specific heat capacity.

$$\Rightarrow S_2 - S_1 = m. Cp. \log_e \frac{T^2}{T^1} - mR \log_e \frac{P^2}{P^1}$$

Change in Entropy for Adiabatic Process

From definition of entropy,

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

For adiabatic process, $\delta Q = 0$

Hence,
$$dS \ge 0$$

For reversible adiabatic process, dS = 0

- $\Rightarrow S = constant$
- ⇒ Constant entropy/Isentropic process

Relationship between Temperature, Pressure and Volume for Isentropic Process

Change in entropy for reversible process can be written as:

$$\Rightarrow$$
 S₂ - S₁ = m. Cv. $\log_e \frac{T^2}{T_1} + mR \log_e \frac{V^2}{V_1}$(i)

$$\Rightarrow S_2 - S_1 = m. Cp. \log_e \frac{T^2}{T_1} - mR \log_e \frac{P^2}{P_1}$$
...(ii)

For reversible adiabatic process $(S_1=S_2)$, equation (i) reduces to:

$$m.Cv.\log_e \frac{T2}{T1} + mR\log_e \frac{V2}{V1} = 0$$

Or,
$$m. Cv. \log_e \frac{T^2}{T^1} = -mR \log_e \frac{V^1}{V^2}$$

Or,
$$Cv \cdot \log_e \frac{T2}{T1} = R \log_e \frac{V1}{V2}$$

Or,
$$\log_e \left(\frac{T2}{T1}\right) \land (C_V) = \log_e \left(\frac{V1}{V2}\right) \land R$$

Or,
$$\left(\frac{T2}{T1}\right) \land (C_V) = \left(\frac{V1}{V2}\right) \land R$$

Or,
$$\left(\frac{T2}{T1}\right) = \left(\frac{V1}{V2}\right) \wedge (R/C_V)$$

Or,
$$\left(\frac{T2}{T1}\right) = \left(\frac{V1}{V2}\right) \wedge \left(C_p - C_v / C_v\right) = \left(\frac{V1}{V2}\right) \wedge (\gamma - 1)$$

Hence,
$$\left(\frac{T^2}{T_1}\right) = \left(\frac{V^1}{V^2}\right) \wedge (\gamma - 1)$$
(iii)

Similarly, for isentropic process, equation (ii) reduces to:

$$\left(\frac{T^2}{T^1}\right) = \left(\frac{P^1}{P^2}\right) \wedge \left[(\gamma-1)/\gamma\right] \dots (iv)$$

From (iii) and (iv)

$$PV^{\gamma} = Constant$$

Change in Entropy for Liquid/Solid Water/Ice/Incompressible Substance

Using Conservation of Energy Equation,

$$\delta Q - \delta W = dU....(i)$$

From definition of entropy for reversible process,

$$dS = \frac{\delta Q}{T} \dots (ii)$$

From (i) and (ii),

$$T.dS = \delta W + dU$$

Or,
$$T. dS = P. dV + dU$$
.....(iii)

For an incompressible substance, $V_1=V_2$ Hence, dV=0

Equation (iii) becomes

$$T.dS = dU$$

Or,
$$T. dS = m. c. dT$$

Or,
$$dS = m.c.\frac{dT}{T}$$

Integrating both sides,

$$\int_{S1}^{S2} dS = m.c. \int_{T1}^{T2} \frac{dT}{T}$$

Or,
$$S_2 - S_1 = m. c. \log_e \frac{T_2}{T_1}$$

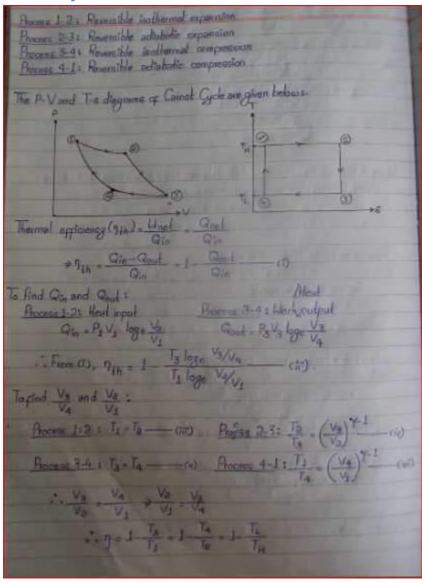
For constant temperature heat exchange, entropy change can be written as

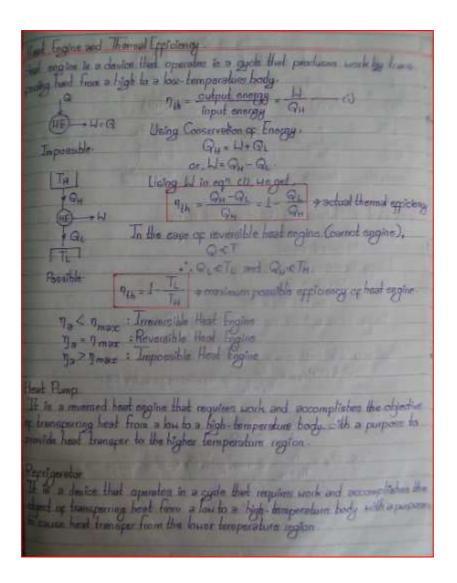
$$dS = \frac{\delta Q}{T}$$

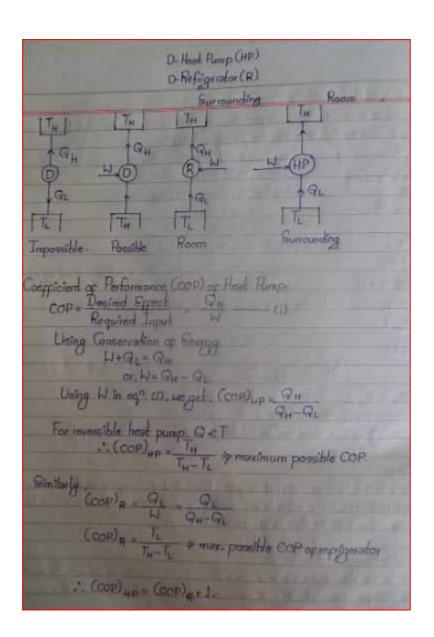
Integrating both sides,

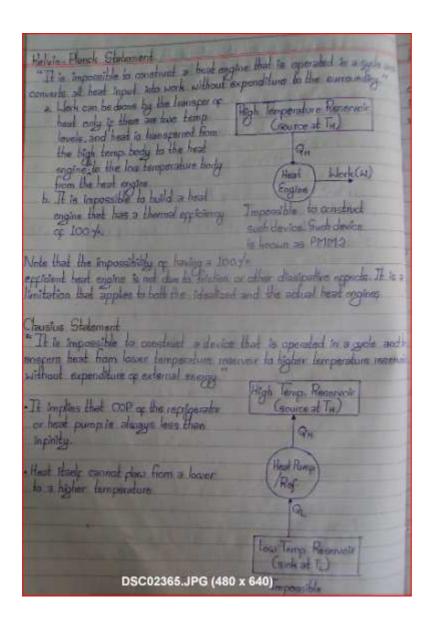
$$S_2 - S_1 = \frac{Q(net)}{T} = \frac{mL}{T}$$

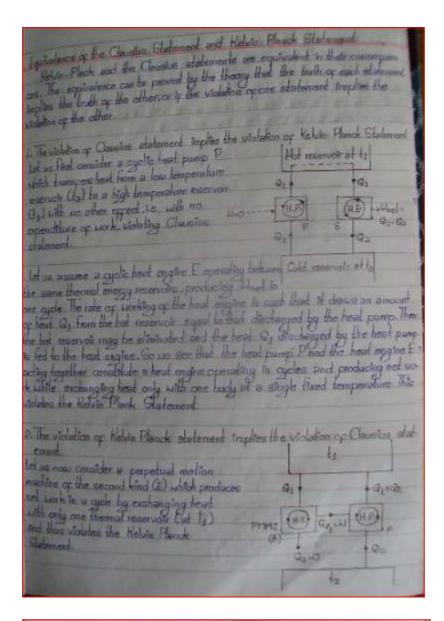
Carnot Cycle





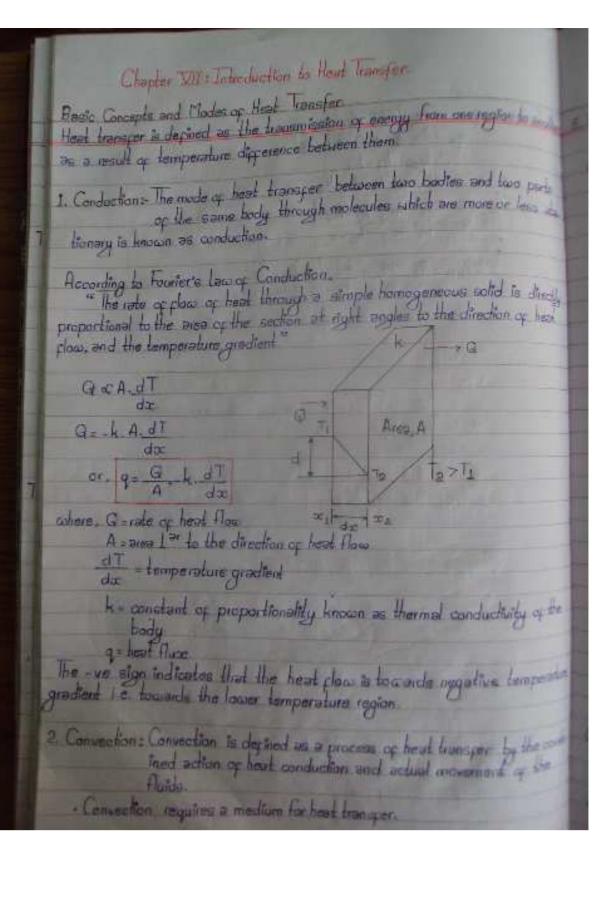




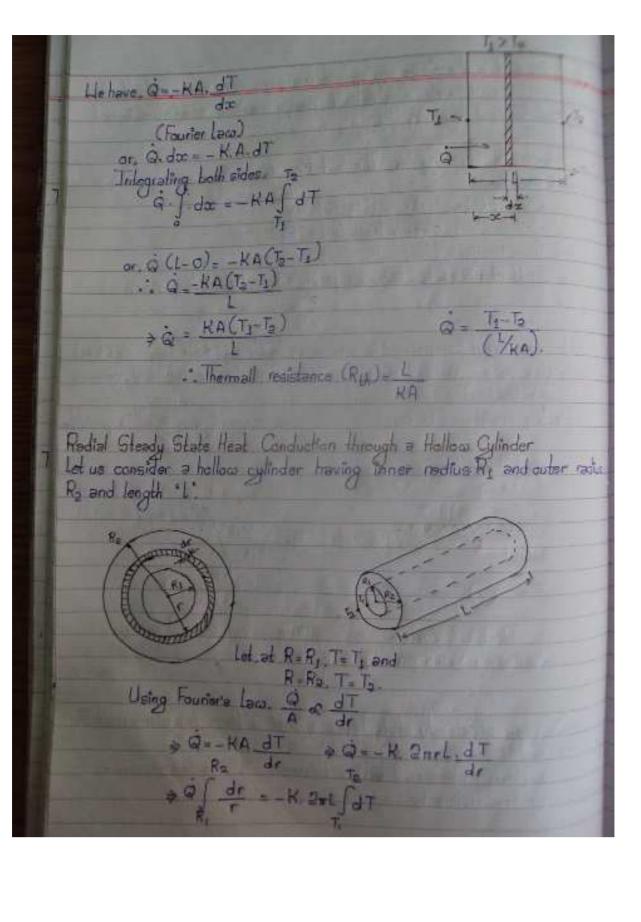


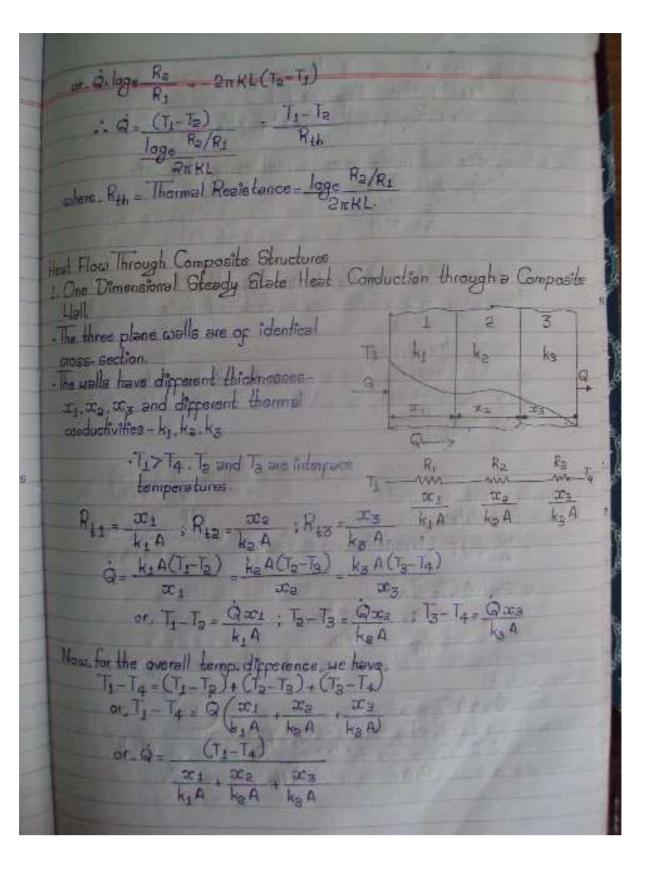
Let us assume a cyclic heat pump(P) extracting heat Qo from a low tring use reservoir at to and discharging heat to the high temperature reservoir to with the expenditure or much it equal to what the PMM2 delivers in a complete cycle. So E and P together constitute a heat pump working in case and producing the sole effect of those arring heat from a lover to a higher perature body, thus violating the Chartes statement.

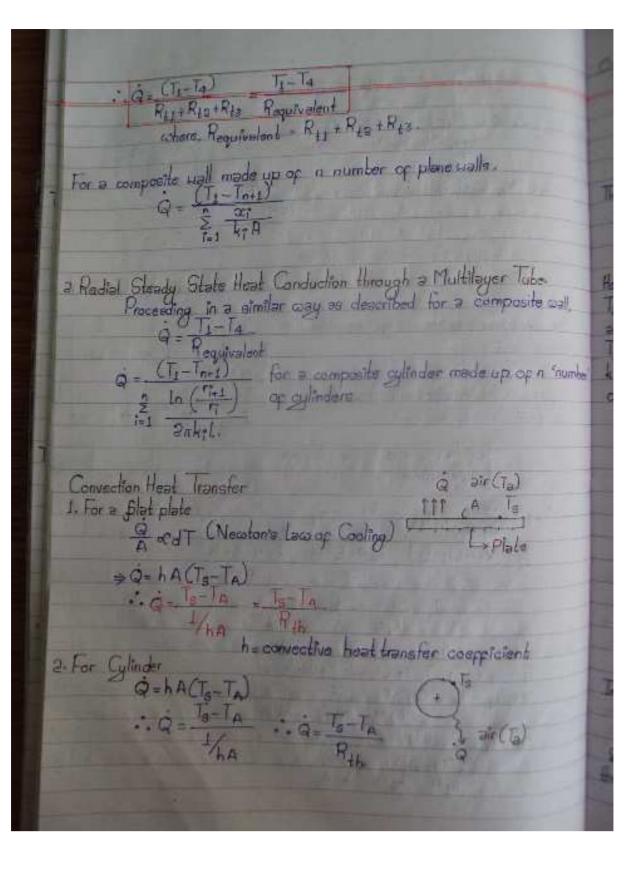
Introduction to Heat Transfer

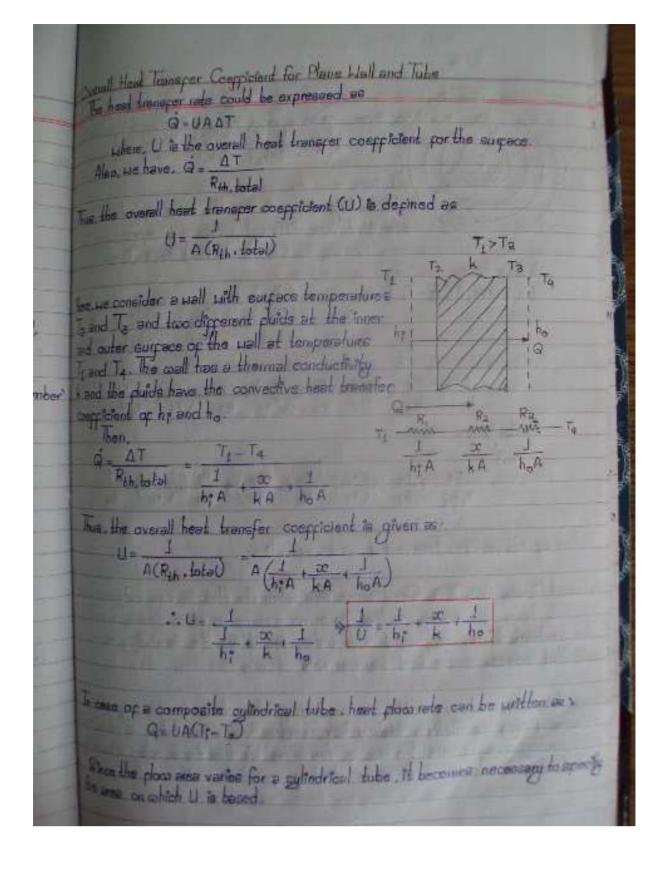


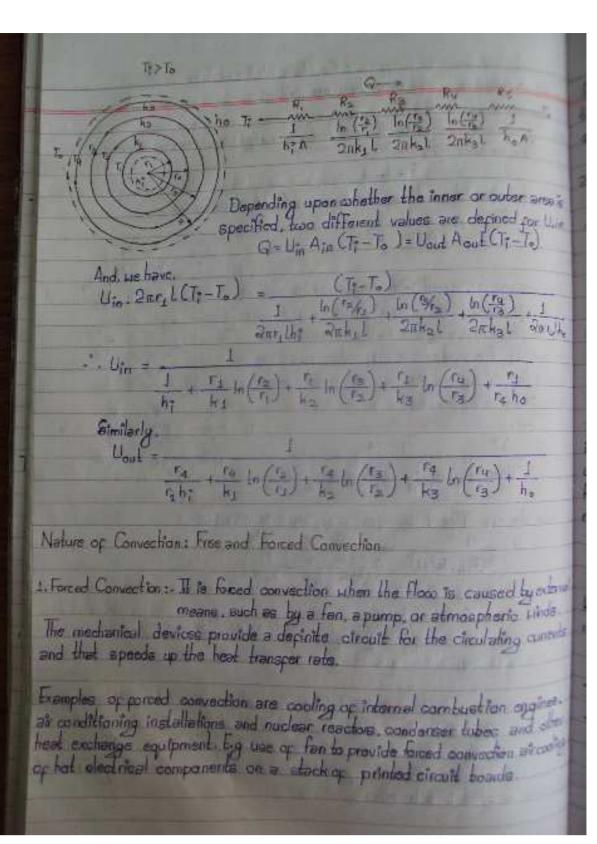
Redistions: It is the phenomen up heat transper from the source to the rever without heating the intervening medium is medium is not equited for heat honefor. Electrical Analogy for Thermal Resistance. Timo Chm's Law. Current (1) = Voltage Potential (dV) Electric Resintance (Re) And from Fourier's Law. Heat flow rate (Q) - Temperature Potential (At) · Hectric current (amperes) is analogous to thermal heat flow rate (KN). · Electric voltage (volta) is analogous to thormal temperature difference (deg. Colsius) · Electric resistance (Chins) is analogous to quantity do This quantity is called thermal resistance WWW Rth = doc Electrical System Equivalent thermal circuit. Thornol Resistance (Rep.) - dec Ine dimensional stoady state heat conduction, through a plane wall flat consider a plene well having thickness "L' melde temperature Is edatoide temperature 12.











and convertion depends on the pollowing properties manufy viscosity design and conductivity, specific hooks temperature dipperence between child and ware fluid velocity, and characteristic linear dimension. he Convection: Fire (or natural) convection is the mode or heat transfer to which the claw is induced by buggancy forces that arise from ently digrerences caused by temperature variations In the skild. Examples: 168 in oching of transmission lines, electric transformers and rectifiers; heat of rome Wite wer of radiators; heat transper from hot pipes and owns surrounded by cooler Winted Circuit Beards Cold the free convection heat transper that rulha main from hot components on a vertical array as circuit beside in will air. Here, the sir that ment contact with the companionts experiences incress in temperature and honce a reduction I density. Since it is now lighter than the surroand air trugy ancy forces Induce a vartical motion Fluid (air) flow which coarm air ascending from the beards is placed by air inclose of cooler ambient air Heat Radiation to todation is due to the property of matter to emit and to absorb different cher net This of radiation and the fact that an comply space is payently permeable to dien and that the matter allows them to pass more or least upats. Stepen's Lew le lea states that the emissive power of a black body is directly proportional alber the parth power of its absolute temporature 20071991 - Lie to Lin Pa T where Es = emissive power of a black body 1 Stepan Beltzmann constant =5.67X10-8 L/m2K+

