

ENGG. THERMODYNAMICS (ETDy)

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Lecture 1 : **Introduction**

Introduction

The most of general sense of thermodynamics is the study of energy and its relationship to the properties of matter. All activities in nature involve some interaction between energy and matter. Thermodynamics is a science that governs the following:

- Energy and its transformation
- Feasibility of a process involving transformation of energy
- Feasibility of a process involving transfer of energy
- Equilibrium processes

More specifically, thermodynamics deals with energy conversion, energy exchange and the direction of exchange.

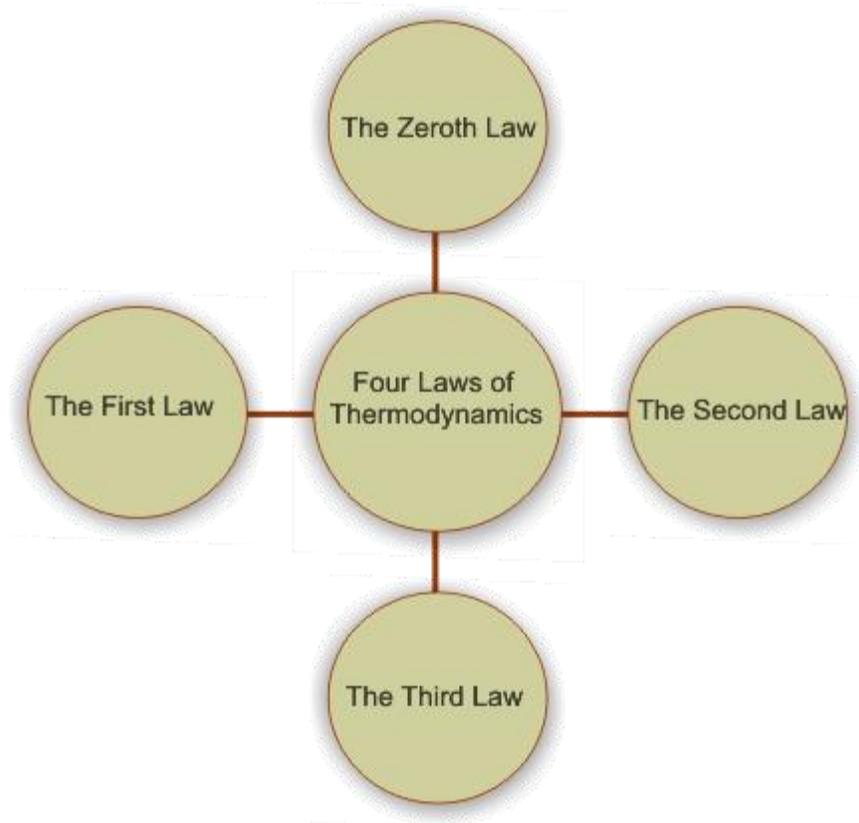
Areas of Application of Thermodynamics:

All natural processes are governed by the principles of thermodynamics. However, the following engineering devices are typically designed based on the principles of thermodynamics.

Automotive engines, Turbines, Compressors, Pumps, Fossil and Nuclear Power Plants, Propulsion systems for the Aircrafts, Separation and Liquefaction Plant, Refrigeration, Air-conditioning and Heating Devices.

The principles of thermodynamics are summarized in the form of a set of axioms. These axioms are known as four thermodynamic laws:

The zeroth law, the first law, the second law and the third law.



- **The Zeroth Law** deals with thermal equilibrium and provides a means for measuring temperatures.
- **The First Law** deals with the conservation of energy and introduces the concept of internal energy.
- **The Second Law** of thermodynamics provides with the guidelines on the conversion of internal energy of matter into work. It also introduces the concept of entropy.
- **The Third Law** of thermodynamics defines the absolute zero of entropy. The entropy of a pure crystalline substance at absolute zero temperature is zero.

Different Approaches in the Study of Thermodynamics

Thermodynamics can be studied through two different approaches:

(a) Macroscopic Approach and

(b) Microscopic Approach

Macroscopic Approach

Consider a certain amount of gas in a cylindrical container. The volume (V) can be measured by measuring the diameter and the height of the cylinder. The pressure (P) of the gas can be measured by a pressure gauge. The temperature (T) of the gas can be measured using a thermometer. The state of the gas can be specified by the measured P , V and T . The values of these variables are space averaged characteristics of the properties of the gas under consideration. In classical thermodynamics, we often use this macroscopic approach. The macroscopic approach has the following features.

- The structure of the matter is not considered.
- A few variables are used to describe the state of the matter under consideration.
- The values of these variables are measurable following the available techniques of experimental physics.

Microscopic Approach

On the other hand, the gas can be considered as assemblage of a large number of particles each of which moves randomly with independent velocity. The state of each particle can be specified in terms of position coordinates (x_i, y_i, z_i) and the momentum components (p_{xi}, p_{yi}, p_{zi}). If we consider a gas occupying a volume of 1 cm^3 at ambient temperature and pressure, the number of particles present in it is of the order of 10^{20} . The same number of position coordinates and momentum components are needed to specify the state of the gas. The microscopic approach can be summarized as:

- A knowledge of the molecular structure of matter under consideration is essential.
- A large number of variables are needed for a complete specification of the state of the matter.

SI Units

SI is the abbreviation of *Système International d' Unités*. The SI units for mass, length, time and force are kilogram, meter, second and newton respectively. The unit of length is meter, m, defined as

1 650 763.73 wavelengths in vacuum of the radiation corresponding to the orange-red line of the spectrum of Krypton-86. The unit of time is second, s. The second is defined as the duration of

9 192 631 770 cycles of the radiation associated with a specified transition of the Cesium 133 atom. The unit of mass is kilogram, kg. It is equal to the mass of a particular cylinder of platinum-iridium alloy kept at the International Bureau of Weights and Measures. The amount of substance can also be expressed in terms of the mole (mol). One kilomole of a

substance is the amount of that substance in kilograms numerically equal to its molecular weight. The number of kilomoles of a substance, n , is obtained by dividing the mass (m) in kilograms by the molecular weight (M), in kg/ kmol.

$$n = \frac{m}{M}$$

The unit for temperature is Kelvin, K . One K is the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water. Quite often the Celsius, $^{\circ}C$, is used to express the temperature of a substance.

$$^{\circ}C = K - 273.16$$

The SI unit of force, called the newton, N is a secondary unit. The, N , is the force required to accelerate a mass of 1 kilogram at the rate of 1 meter per (second)².

$$1 N = (1\text{kg}) (1\text{m/s}^2) = 1\text{kg m/s}^2$$

The smaller or bigger quantities are expressed using the following prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{12}	tera	T	10^{-2}	centi	c
10^9	giga	G	10^{-3}	milli	m
10^6	mega	M	10^{-6}	micro	μ
10^3	kilo	k	10^{-9}	nano	n
10^2	hecto	h	10^{-12}	pico	p

Pressure

Pressure is the normal force exerted by a system against unit area of the boundary surface.

$$P = \lim_{\delta A \rightarrow 0} \frac{\delta F_n}{\delta A}$$

where δA approaches zero.

The unit for pressure in SI is pascal, Pa

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

Two other units are widely used

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa} = 0.1 \text{ MPa}$$

and the standard atmosphere, where

$$1 \text{ atm} = 101.325 \text{ kPa} = 1.01325 \text{ bar} = \text{pressure exerted by a column of 760 mm of Hg}$$

Energy

Energy is the capacity to exert a force through a distance. In SI, the unit of energy is Newton-meter, N m or Joule, J.

Power

The rate of energy transfer or storage is called power. The unit of power is watt, W.

$$1 \text{ W} = 1 \text{ J/s} = 1 \text{ N m/s} \text{ and } 1 \text{ kW} = 1000 \text{ W.}$$

Apart from

these, the

following units are

used for

various parameters

of interest

Frequency, Hertz = $\text{Hz} = \text{s}^{-1}$

Electric current, Ampere = A

Electric charge, Coulomb, C = As

Electric potential, Volt = $\text{V} = \text{W/A}$

Magnetic flux, Weber, $\text{Wb} = \text{Vs}$

Magnetic flux density, Tesla, $\text{T} = \text{Wb/m}^2$

Lecture 2 : System, Surroundings and Properties

The lecture deals with

- System
- Surroundings
- Types of Systems
- Intensive and Extensive Properties

System

A thermodynamic system is defined as a definite quantity of matter or a region in space upon which attention is focused in the analysis of a problem. We may want to study a quantity of matter contained within a closed rigid walled chamber, or we may want to consider something such as gas pipeline through which the matter flows. The composition of the matter inside the system may be fixed or may change through chemical and nuclear reactions. A system may be arbitrarily defined. It becomes important when exchange of energy between the system and the everything else outside the system is considered. The judgement on the energetics of this exchange is very important.

Surroundings

Everything external to the system is surroundings. The system is distinguished from its surroundings by a specified boundary which may be at rest or in motion. The interactions between a system and its surroundings, which take place across the boundary, play an important role in thermodynamics. A system and its surroundings together comprise a universe.

Types of systems

Two types of systems can be distinguished. These are referred to, respectively, as closed systems and open systems or control volumes. A closed system or a control mass refers to a fixed quantity of matter, whereas a control volume is a region in space through which

mass may flow. A special type of closed system that does not interact with its surroundings is called an **Isolated system** .

Two types of exchange can occur between the system and its surroundings:

1. energy exchange (heat or work) and
2. exchange of matter (movement of molecules across the boundary of the system and surroundings).

Based on the types of exchange, one can define

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

If the boundary does not allow heat (energy) exchange to take place it is called adiabatic boundary otherwise it is diathermal boundary.

Property

To describe a system and predict its behaviour requires a knowledge of its properties and how those properties are related. Properties are macroscopic characteristics of a system such as mass, volume, energy, pressure and temperature to which numerical values can be assigned at a given time without knowledge of the past history of the system. Many other properties are considered during the course of our study.

- The value of a property of a system is independent of the process or the path followed by the system in reaching a particular state.
- The change in the value of the property depends only on the initial and the final states.

The word state refers to the condition of a system as described by its properties.

Mathematically, if P is a property of the system, then the change in the property in going from the initial state 1 to the final state 2 is given by

$$\int_1^2 dP = P_2 - P_1$$

If $P = P(x, y)$ then,

$$dP = \left(\frac{\partial P}{\partial x} \right)_y dx + \left(\frac{\partial P}{\partial y} \right)_x dy = a dx + b dy$$

where,

$$a = \left(\frac{\partial P}{\partial x} \right)_y \text{ and } b = \left(\frac{\partial P}{\partial y} \right)_x$$

If $\left(\frac{\partial a}{\partial y} \right)_x = \left(\frac{\partial b}{\partial x} \right)_y$, then dP is said to be an exact differential, and P is a point function. A thermodynamic property is a point function and not a path function. Pressure, temperature, volume or molar volume are some of the quantities which satisfy these requirements.

Intensive and Extensive Properties

There are certain properties which depend on the size or extent of the system, and there are certain properties which are independent of the size or extent of the system. The properties like volume, which depend on the size of the system are called extensive properties. The properties, like temperature and pressure which are independent of the mass of the system are called **intensive properties**. The test for an intensive property is to observe how it is affected when a given system is combined with some fraction of exact replica of itself to create a new system differing only by size. Intensive properties are those which are unchanged by this process, whereas those properties whose values are increased or decreased in proportion to the enlargement or reduction of the system are called extensive properties.

Assume two identical systems S_1 and S_2 as shown in Figure 2.1 . Both the systems are in identical states.

Let S_3 be the combined system. Is the value of property for S_3 same as that for S_1 (and S_2)?

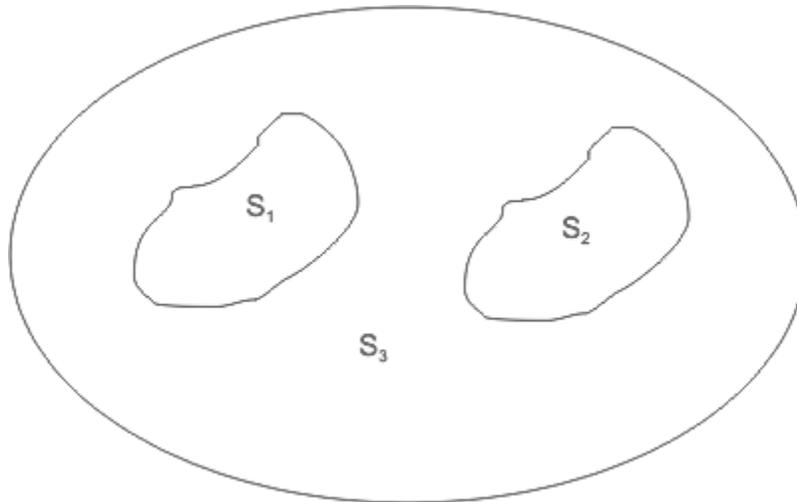


Figure 2.1

- If the answer is yes, then the property is intensive
- If the answer is no, then the property is extensive

The ratio of the extensive property to the mass is called the specific value of that property

specific volume, $v = V/m = 1/\rho$ (ρ is the density)

specific internal energy, $u = U/m$

Similarly, the molar properties are defined as the ratios of the properties to the mole number (N) of the substance

Molar volume = $\hat{v} = V/N$

Molar internal energy = $\hat{u} = U/N$

Lecture 3 : Energy and Processes

The lecture deals with

- Energy
- Macroscopic modes of Energy
- Microscopic modes of Energy
- Thermodynamic Equilibrium
- Process

Energy

Energy is often defined as the capacity to produce work. However, this "capacity" has a special significance. The capacity represents a combination of an effort and the change brought about by the effort. However, the effort is exerted in overcoming resistance to a particular type of change.

The effort involved is measured quantitatively as a "driving force" in thermodynamics. A driving force is a property which causes and also controls the direction of change in another property. The quantitative value of this change is called a "**displacement**". The product of a driving force and its associated displacement represents a quantity of energy, but in thermodynamics this quantity has meaning only in relation to a specifically defined system.

Relative to a particular system there are generally two ways of locating a driving force and the displacement it produces. In one way, the driving force and the displacement are properties of the system and are located entirely within it. The energy calculated from their product represents a change in the internal energy of the system. Similarly, both the driving force and its displacement could be located entirely within the surroundings so that the calculated energy is then a change in the total energy of the surroundings.

In another way, the displacement occurs within the system but the driving force is a property of the surroundings and is applied externally at the system boundary. By definition, the boundary of a system is a region of zero thickness containing no matter at all so that the energy calculated in this way is not a property of matter either in the system or in its surroundings but represents a quantity of energy in transition between the two. In any quantitative application of thermodynamics it is always important to make a careful

distinction between energy changes within a system or within its surroundings and energy in transition between them.

Macroscopic modes of energy

- **Kinetic Energy (KE)**

If a body is accelerated from its initial velocity V_1 to final velocity V_2 , the total work done on the body is

$$W = \int_1^2 mVdV = \frac{m(V_2^2 - V_1^2)}{2} = \frac{\Delta(mV^2)}{2}$$

The work done on a body in accelerating it from its initial velocity V_1 to a final velocity V_2 , is equal to the change in the kinetic energy of the body. If the body is decelerated from a velocity V_2 to a velocity V_1 by the application of resisting force, the work done by the body is equal to decrease in its kinetic energy.

- **Potential Energy (PE)**

- A body of mass m is moved from an initial elevation Z_1 to a final elevation Z_2 (Fig 3.1)

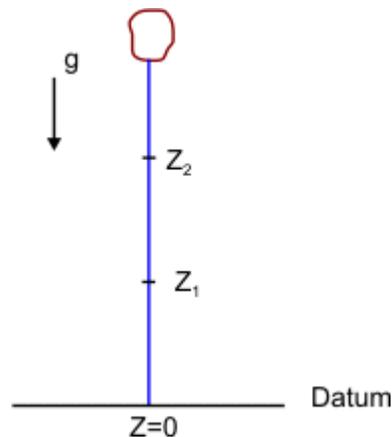


Figure 3.1

- The force on the body, $F = mg$
- This force has moved a distance $(Z_2 - Z_1)$. Therefore, the work done on the body

$$W = F (Z_2 - Z_1) = mg(Z_2 - Z_1) = \Delta(mgZ)$$



The kinetic energy and potential energy are also called organized form of energy that can be readily converted into work.

Microscopic modes of energy

The microscopic modes of energy refer to the energy stored in the molecular and atomic structure of the system.

The molecules are in random motion. A molecule possesses energy in several forms.

- Translational energy, Rotational energy, Vibrational energy.
- Electronic energy, Chemical energy, Nuclear energy.

If ε represents energy of one molecule, then

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vid} + \varepsilon_{elec} + \varepsilon_{chem} + \varepsilon_{nucl}$$

If N is the total number of molecules in the system, then the total amount of microscopic form of energy

$$U = N \varepsilon$$

We may also call this as INTERNAL ENERGY of the system. The internal energy, U is due to random motions or disorganized motions of molecules. The internal energy cannot be readily converted into work. One of the major tasks involved in thermodynamics is devising means for converting disorganized internal energy into useful or organized work.

Thermodynamic Equilibrium

Steady state

Under the steady state condition, the properties of the system at any location are independent of time.

Equilibrium

At the state of equilibrium, the properties of the system are uniform and only one value can be assigned to it.

In thermodynamics, equilibrium refers to a state of equilibrium with respect to all possible changes, thermal, mechanical and chemical.

a. Thermal equilibrium

A state of thermal equilibrium can be described as one in which the temperature of the system is uniform.

b. Mechanical equilibrium

Mechanical equilibrium means there is no unbalanced force. In other words, there is no pressure gradient within the system.

c. Chemical equilibrium

The criterion for chemical equilibrium is the equality of chemical potential

$$\mu_i^A = \mu_i^B$$

Superscripts A and B refers to systems and subscript i refers to component

If Gibbs function is given by G , $G = U + PV - TS$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{n_j (j \neq i)}$$

where n_i is the number of moles of substance i . The composition of a system does not undergo any change because of chemical reaction

Process

In thermodynamics we are mainly concerned with the systems which are in a state of equilibrium. Whenever a system undergoes a change in its condition, from one equilibrium state to another equilibrium state, the system is said to undergo a process.

Consider a certain amount of gas enclosed in a piston-cylinder assembly as our system. Suppose the piston moves under such a condition that the opposing force is always infinitesimally smaller than the force exerted by the gas. The process followed by the system is **reversible**.

A process is said to be reversible if the system and its surroundings are restored to their respective initial states by reversing the direction of the process. A reversible process has to be quasi-static, but a quasi - static process is not necessarily quasi-static.

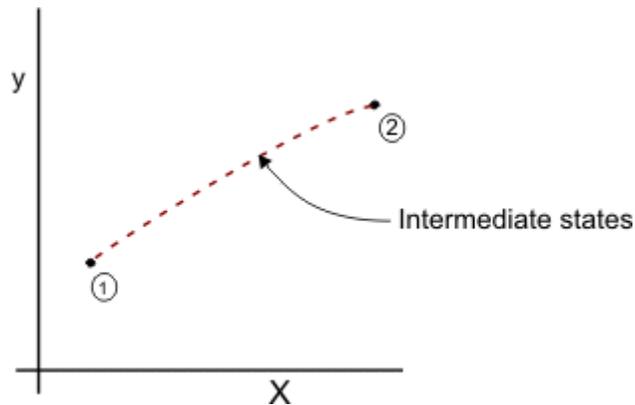


Figure 3.2

The process is irreversible if it does not fulfil the criterion of reversibility. Many processes are characterized by the fact that some property of the system remains constant. These processes are:

A process in which the volume remains constant

- constant volume process. Also called **isochoric process / isometric process**

A process in which the pressure of the system remains constant.

- constant pressure process. Also called **isobaric process**

A process in which the temperature of the system is constant.

- constant temperature process. Also called **isothermal process**

A process in which the system is enclosed by adiabatic wall.

- **Adiabatic process**

Lecture 4 : **Work and Heat**

The lecture deals with

- Work
- Thermodynamic Definition of Work
- Heat

Work

Work is one of the basic modes of energy transfer. The work done by a system is a path function, and not a point function. **Therefore, work is not a property of the system, and it cannot be said that the work is possessed by the system.** It is an interaction across the boundary. What is stored in the system is energy, but not work. A decrease in energy of the system appears as work done. **Therefore, work is energy in transit and it can be identified only when the system undergoes a process.**

Work must be regarded only as a type of energy in transition across a well defined, zero thickness, boundary of a system. Consequently work, is never a property or any quantity contained within a system. Work is energy driven across by differences in the driving forces on either side of it. Various kinds of work are identified by the kind of driving force involved and the characteristic extensive property change which accompanied it. Work is measured quantitatively in the following way. Any driving force other than temperature, located outside the system on its external boundary, is multiplied by a transported extensive property change within the system which was transferred across the system boundary in response to this force. The result is the numerical value of the work

associated with this system and driving force. In static Equilibrium, $F=PA$ (Fig 4.1). The dX is small so that P does not change. The change in volume of the gas = AdX . The elemental work,

$$dW = FdX = PAdX = PdV$$

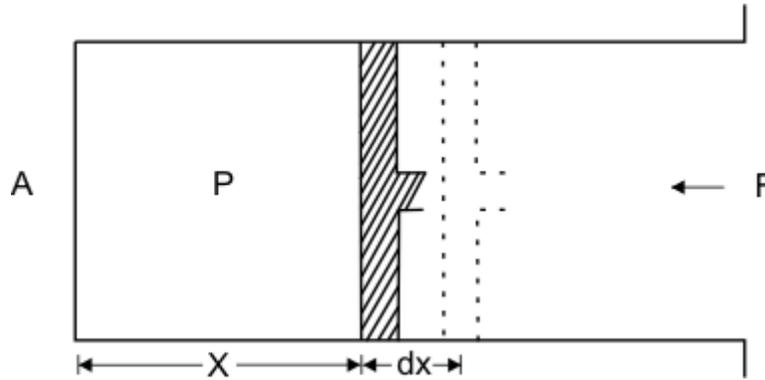


Figure 4.1

Thermodynamic Definition of Work

In thermodynamics, work done by a system on its surroundings during a process is defined as that interaction whose sole effect, external to the system, could be reduced as the raising of a mass through a distance against gravitational force. Let us consider the raising of mass m from an initial elevation z_1 to final elevation z_2 against gravitational force. To raise this mass, the force acting on the mass is given by $F = mg$. The work done on the body is $W = mg(z_2 - z_1)$

- An external agency is needed to act on the system
- It can be seen that expansion of the gas gets reduced to raising a mass against gravitational force (Figure 4.2)

$$dW = F dX = P A dX = P dV$$

$$W = \int_1^2 PdV$$

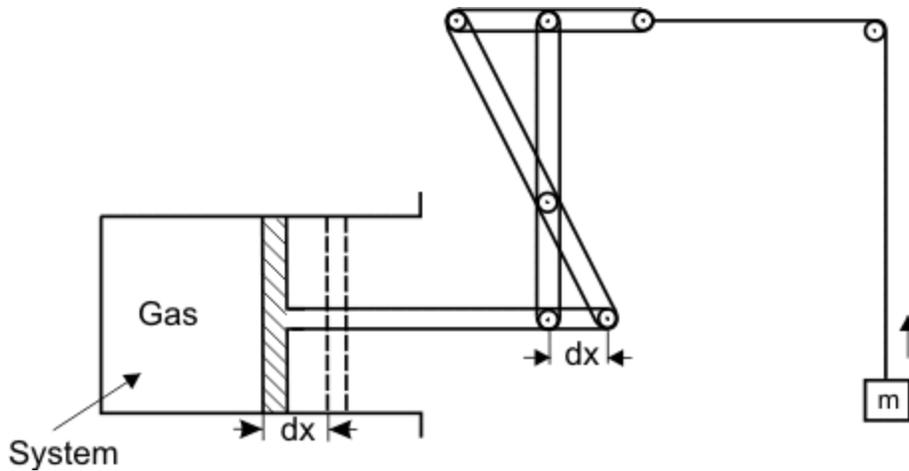


Figure 4.2

During this expansion process, the external pressure is always infinitesimally smaller than the gas pressure.

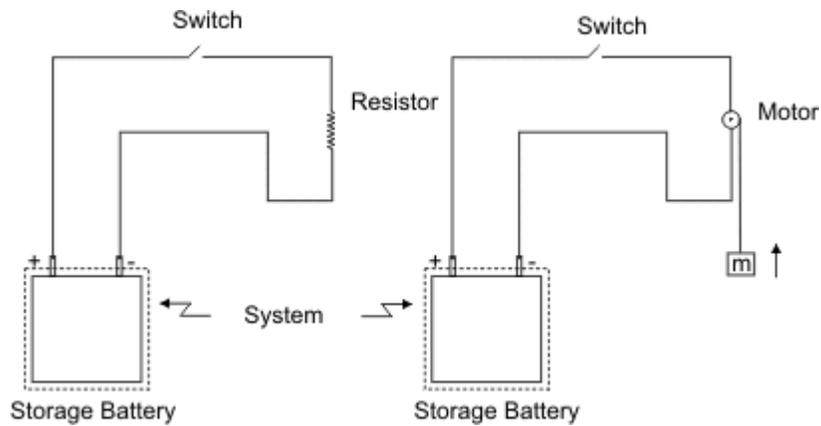


Figure 4.3

Compare two systems shown in the figure 4.3. Let the resistor be replaced by a motor drawing the same amount of current as the resistor. The motor can wind a string and thereby raise the mass which is suspended. As far as the battery is concerned, the situations are identical. So, according to thermodynamic definition of work, the interaction of a battery with a resistor is called work. By manipulating the environment, that is external to the battery (system), the effect can be reduced to raising of a mass against the gravitational force and that is the only effect on the surroundings. We can see that the thermodynamic definition of work is more general than that used in mechanics.

Situation in which $W \neq P dV$

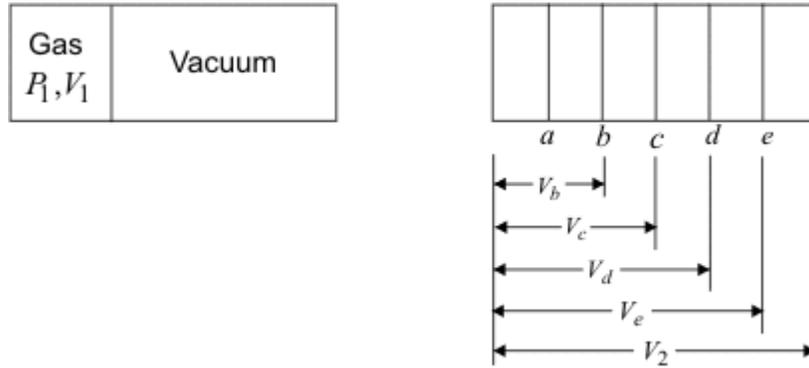


Figure 4.4

- Let the initial volume be V_1 and pressure P_1
- Let the final volume be V_2 and pressure P_2

What should be the work done in this case? Is it equal to $\int P dV$?

$\int P dV =$ area under the curve indicating the process on P - V diagram.

The expansion process may be carried out in steps as shown in figure 4.4. It is possible to draw a smooth curve passing through the points $1bcde2$. Does the area under the curve (figure 4.5) represent work done by the system? The answer is no, because the process is not reversible. The expansion of the gas is not restrained by an equal and opposing force at the moving boundary.

$$W \neq \int P dV$$

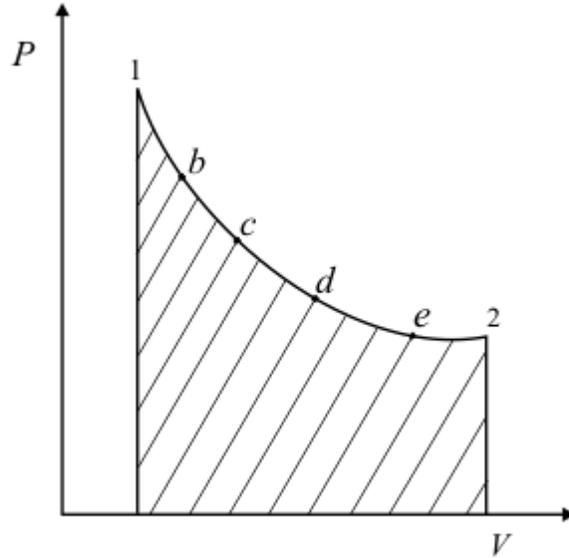


Figure 4.5

No external force has moved through any distance in this case, the work done is zero. Therefore, we observe that

$$W = \int P dV \text{ only for reversible process}$$

$$W \neq \int P dV \text{ for an irreversible process}$$

Another exceptional situation !

- The piston is held rigid using latches ! (Figure 4.6)
- $dV = 0$
- Work done on the gas is equal to the decrease in the potential energy of mass m
- A situation where $dV = 0$ and yet dW is not zero
- such work can be done in one direction only. Work is done on the system by the surroundings

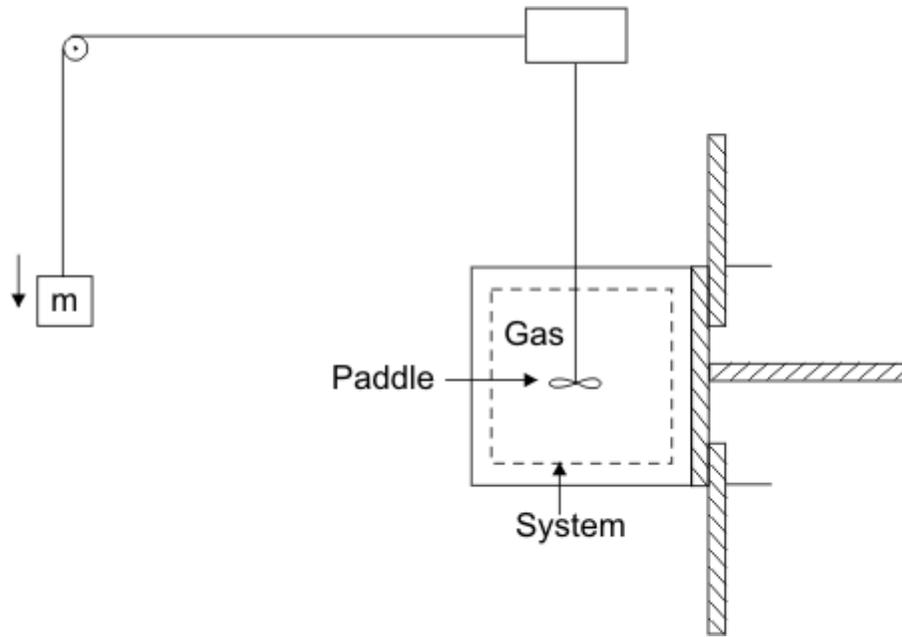


Figure 4.6

Heat

Heat is energy transfer which occurs by virtue of temperature difference across the boundary. Heat like work, is energy in transit. It can be identified only at the boundary of the system. Heat is not stored in the body but energy is stored in the body. Heat like work, is not a property of the system and hence its differential is not exact. Heat and work are two different ways of transferring energy across the boundary of the system.

The displacement work is given by (figure 4.7)

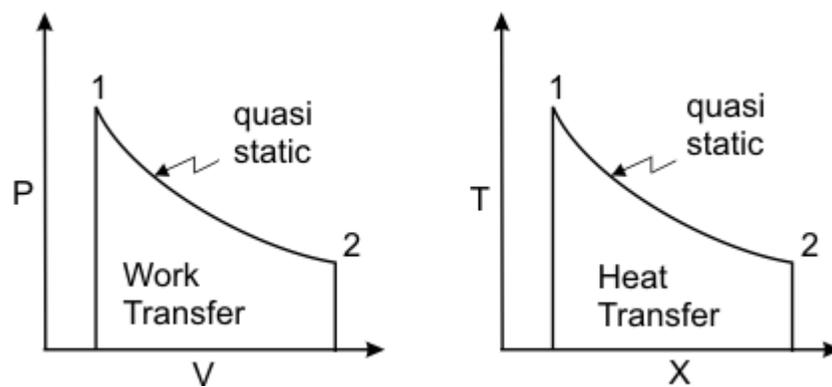


Figure 4.7

$$W_{1-2} = \int_1^2 dW = \int_1^2 PdV$$

It is valid for a quasi-static or reversible process. The work transfer is equal to the integral of the product of the intensive property P and the differential change in the extensive property, dV .

Just like displacement work, the heat transfer can also be written as

$$Q_{1-2} = \int_1^2 TdX = \int_1^2 dQ$$

The quantity dQ is an inexact differential.

$$dQ = TdX$$

X is an extensive property and dX is an exact differential. The extensive property is yet to be defined. We shall see later that X is nothing but the entropy, S of a system.

It is possible to write

$$dX = \frac{1}{T}dQ$$

or,

$$\int_1^2 dX = \int_1^2 \frac{1}{T}dQ$$

where $\frac{1}{T}$ is integrating factor.

Lecture 5 : State Postulate and Zeroth- Law of Thermodynamics

The lecture deals with

- Introduction to state postulate
- Zeroth Law of Thermodynamics
- Temperature Scale
- Perfect Gas Scale

Introduction to state postulate

Since every thermodynamic system contains some matter with energy in its various forms, the system can be completely described by specifying the following variables.

- The composition of the matter in terms of mole numbers of each constituent.
- The energy of the system.
- The volume of the system, and
- The measurable properties, such as pressure and temperature.

By specifying these quantities, the state of the system is defined. Once the system is in a given state, it possesses a unique state of properties like pressure, P , temperature, T , density, etc. All the properties of a system cannot be varied independently since they are interrelated through expressions of the following type

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

For example, the pressure, temperature and molar volume (v) of an ideal gas are related by the expression $Pv = RT$. Here R is a constant. Only two of the three variables P , v and T can be varied independently. Question is that for a given thermodynamics system, how many variables can be varied independently.

The State Postulate

As noted earlier, the state of a system is described by its properties. But we know from experience that we do not need to specify all the properties in order to fix a state. Once a

sufficient number of properties are specified, the rest of the properties assume certain values automatically. The number of properties required to fix the state of a system is given by the **state postulate**:

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

A system is called a **simple compressible system** in the absence of electrical, magnetic, gravitational, motion, and surface tension effects. These effects are due to external force fields and are negligible for most engineering problems. Otherwise, an additional property needs to be specified for each effect which is significant. If the gravitational effects are to be considered, for example, the elevation z needs to be specified in addition to the two properties necessary to fix the state.

The state postulate is also known as the **two-property rule**.

The state postulate requires that the two properties specified be **independent** to fix the state. Two properties are independent if one property can be varied while the other one is held constant. Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system (Fig. 5.1).

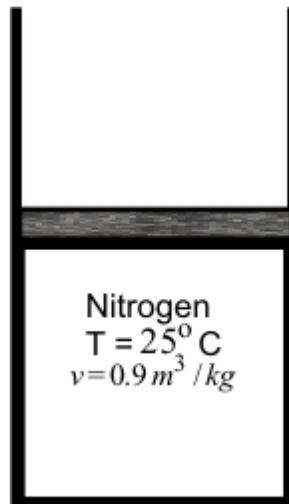


Figure 5.1

For a simple compressible substance (gas), we need the following properties to fix the state of a system:

ρv or PT or vT or uP or uv . Why not u and T ? They are closely related. For ideal gas $u = u(T)$

Temperature and pressure are dependent properties for multi-phase systems. At sea level ($P = 1\text{ atm}$), water boils at 100°C , but on a mountain-top where the pressure is lower, water boils at a lower temperature. That is, $T = f(P)$ during a phase-change process, thus temperature and pressure are not sufficient to fix the state of a two-phase system.

Therefore, by specifying any two properties we can specify all other state properties. Let us choose P and v

Then

$$T = T(P, v)$$
$$u = u(P, v) \text{ etc.}$$

Can we say $W = W(p, v)$

No. Work is not a state property, nor is the heat added (Q) to the system.

Zeroth Law of Thermodynamics

Statement: If a body 1 is in thermal equilibrium with body 2 and body 3, then the body 2 and body 3 are also in thermal equilibrium with each other

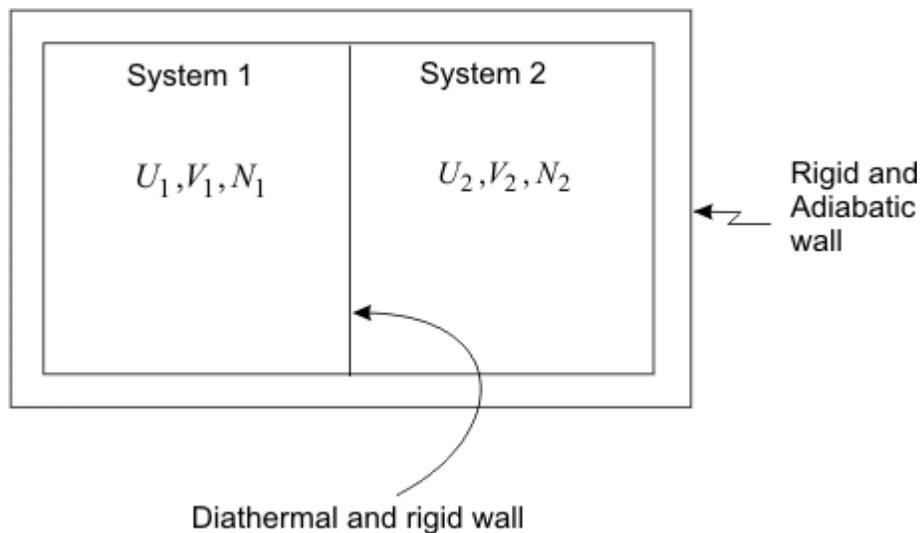


Figure 5.2

Two systems 1 and 2 with independent variables (U_1, V_1, N_1) and (U_2, V_2, N_2) are brought into contact with each other through a diathermal wall (figure 5.2). Let the system 1 be hot and system 2 be cold. Because of interaction, the energies of both the systems, as well as their independent properties undergo a change. The hot body becomes cold and the cold body becomes hot. After sometime, the states of the two systems do not undergo any further change and they assume fixed values of all thermodynamic properties. These two systems are then said to be in a state of thermal equilibrium with each other. The two bodies which are in thermal equilibrium with each other have a common characteristic called temperature. Therefore temperature is a property which has the same value for all the bodies in thermal equilibrium.

Suppose we have three systems 1, 2 and 3 placed in an adiabatic enclosure as shown in figure 5.3.

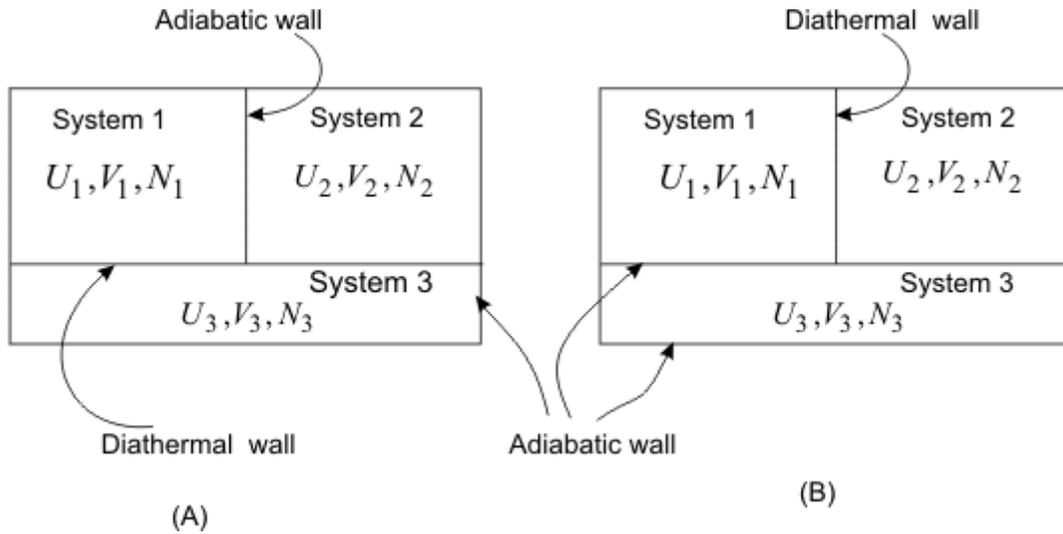


Figure 5.3

The systems 1 and 2 do not interact with each other but they interact separately with systems 3 through a diathermal wall. Then system 1 is in thermal equilibrium with system 3 and system 2 is also in thermal equilibrium with system 3. By intuition we can say that though system 1 and 2 are not interacting, they are in thermal equilibrium with each other.

Suppose system 1 and 2 are brought into contact with each other by replacing the adiabatic wall by a diathermal wall as shown in figure 5.3 (B). Further they are isolated from system 3 by an adiabatic wall. Then one observes no change in the state of the systems 1 and 2.

Temperature Scale

Based on zeroth law of thermodynamics, the temperature of a group of bodies can be compared by bringing a particular body (a thermometer) into contact with each of them in turn. To quantify the measurement, the instrument should have thermometric properties. These properties include: The length of a mercury column in a capillary tube, the resistance (electrical) of a wire, the pressure of a gas in a closed vessel, the emf generated at the junction of two dissimilar metal wires etc. are commonly used thermometric properties.

To assign numerical values to the thermal state of a system, it is necessary to establish a temperature scale on which temperature of a system can be read. Therefore, the

temperature scale is read by assigning numerical values to certain easily reproducible states. For this purpose, it is customary to use

- a. **Ice Point:** The equilibrium temperature of ice with air saturated water at standard atmospheric pressure which is assigned a value of 0°C .
- b. **Steam Point:** The equilibrium temperature of pure water with its own vapor at standard atmospheric pressure, which is assigned a value of 100°C .

This scale is called the **Celsius Scale** named after Anders Celsius.

Perfect Gas Scale

An ideal gas obeys the relation

$$P \hat{v} = R T$$

where R is the Universal Gas Constant ($R = 8.314 \text{ J/mol K}$). This equation is only an approximation to the actual behavior of the gases. The behavior of all gases approaches the ideal gas limit at sufficiently low pressure (in the limit $P \rightarrow 0$). **The perfect gas temperature scale is based on the observation that the temperature of a gas at constant volume increases monotonically with pressure.** If the gas pressure is made to approach zero, the gas behavior follows the relation

$$P \hat{v} = R T$$

Figure 5.4 shows a constant volume gas thermometer.

The bulb is placed in the system whose temperature is to be measured. The mercury column is so adjusted that the level of mercury stands at the reference mark S . This ensures that the volume of the gas is held at a constant value. Let the pressure of the gas be read as P . Let a similar measurement be made when the gas bulb is maintained at the triple point of water, P_{tp} . We can obtain triple point by putting water and ice in an insulated chamber and evacuating air (which is then replaced by water vapour).

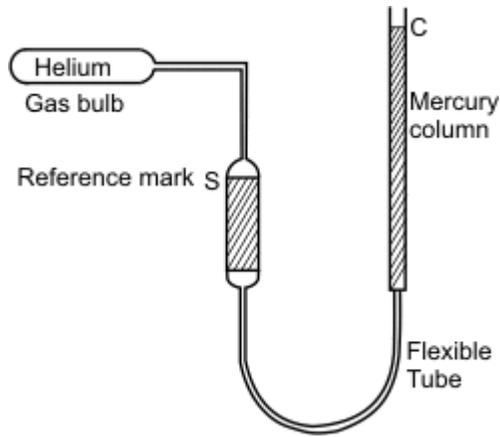


Figure 5.4

The temperature of the triple point of water has been assigned a value of 273.16 K. Since for an ideal gas T varies as P ,

$$\frac{T}{T_{tp}} = \frac{P}{P_{tp}}$$

or,

$$T = 273.16 \frac{P}{P_{tp}}$$

where T_{tp} is the triple point temperature of water.

Suppose a series of measurements with different amounts of gas in the bulb are made. The measured pressures at the triple point as well as at the system temperature change depending on the amount of gas in the bulb. A plot of the temperature T_{cal} , calculated from the expression $T = 273.16 (P / P_{tp})$ as a function of the pressure at the triple point, results in a curve as shown in figure 5.5.

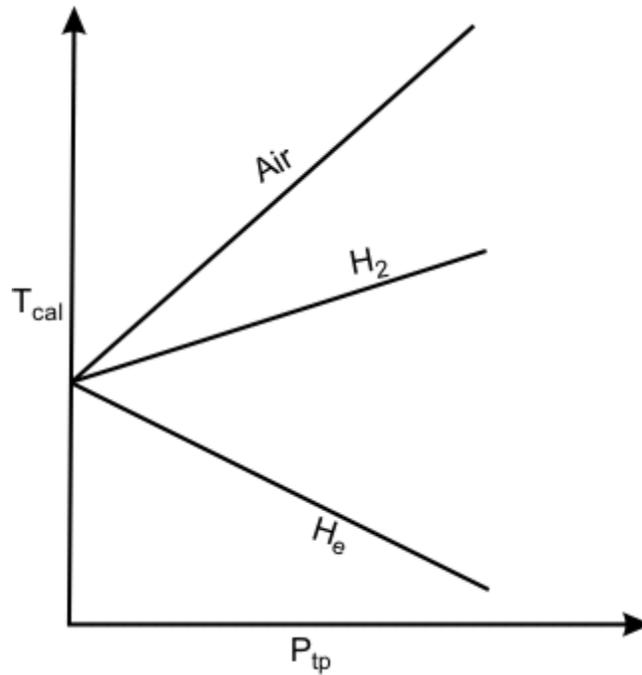


Figure 5.5

When these curves are extrapolated to zero pressure, all of them yield the same intercept. This behaviour can be expected since all gases behave like ideal gas when their pressure approaches zero. The correct temperature of the system can be obtained only when the gas behaves like an ideal gas, and hence the value is to be calculated in limit $P_{tp} \rightarrow 0$. Therefore

$$T = 273.16 \left(\frac{P}{P_{tp}} \right), \text{ as } P_{tp} \rightarrow 0$$

A constant pressure thermometer also can be used to measure the temperature. In that case,

$$T = 273.16 \left(\frac{V}{V_{tp}} \right); \text{ when } V_{tp} \rightarrow 0$$

Here V_{tp} is the volume of the gas at the triple point of water and V is the volume of the gas at the system temperature.

Lecture 6 :

The lecture deals with

- First Law of Thermodynamics
- Heat is a Path Function
- Energy is a Property of the System
- A Perpetual Motion Machine of First Kind
- Analysis of Closed Systems

First Law of Thermodynamics

A series of Experiments carried out by Joule between 1843 and 1848 form the basis for the **First Law of Thermodynamics**

The following are the observations during the Paddle Wheel experiment shown in Fig. 6.1.

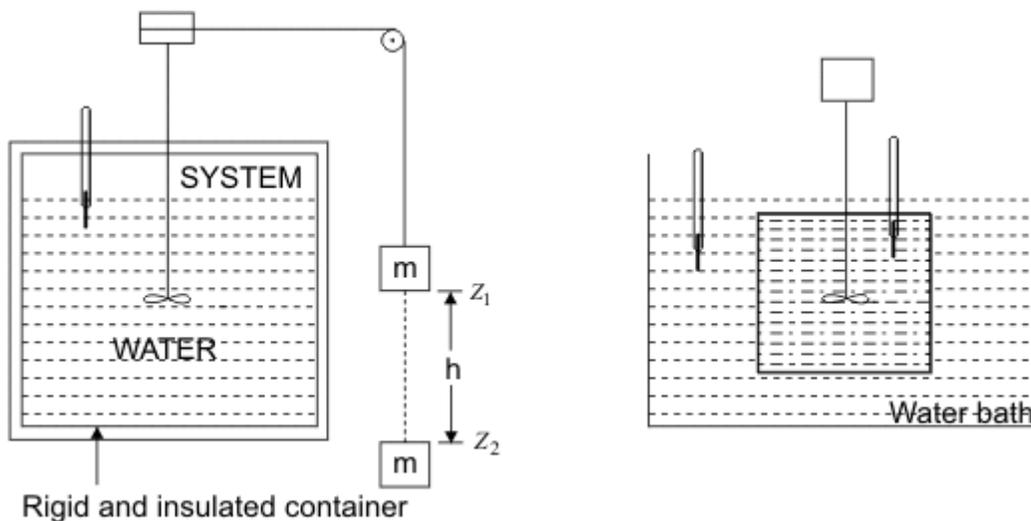


Figure 6.1

- Work done on the system by lowering the mass m through $(z_1 - z_2)$ = change in PE of m

- Temperature of the system was found to increase
- System was brought into contact with a water bath
- System was allowed to come back to initial state
- Energy is transferred as heat from the system to the bath

The system thus executes a cycle which consists of work input to the system followed by the transfer of heat from the system.

$$\oint_{\text{from the system}} dQ = \oint_{\text{on the system}} dW \quad (6.1)$$

Whenever a system undergoes a cyclic change, however complex the cycle may be, the algebraic sum of the work transfer is equal to the algebraic sum of the energy transfer as heat (FIRST LAW OF THERMODYNAMICS).

Sign convention followed in this text:

- **Work done by a system** on its surroundings is treated as a **positive quantity**.
- **Energy transfer as heat to a system** from its surroundings is treated as a **positive quantity**

$$-\oint dQ - \oint (-dW) = \oint dQ - \oint dW = 0 \quad (6.2)$$

or,

$$\oint (dQ - dW) = 0$$

Heat is Path Function

Lets us consider following two cycles: 1a2b1 and 1a2c1 and apply the first law of thermodynamics Eq (6.2) to get

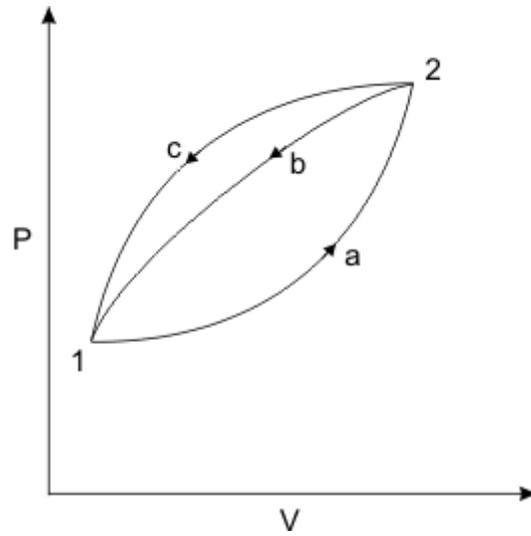


Figure 6.2

$$\int_{1a2} dQ + \int_{2b1} dQ - \int_{1a2} dW - \int_{2b1} dW = 0 \quad (6.3)$$

or,

$$\int_{1a2} dQ + \int_{2c1} dQ - \int_{1a2} dW - \int_{2c1} dW = 0 \quad (6.4)$$

Subtracting Eq. (6.4) from Eq. (6.3)

$$\int_{2b1} dQ - \int_{2c1} dQ - \left(\int_{2b1} dW - \int_{2c1} dW \right) = 0 \quad (6.5)$$

Since, work depends on the path

$$\int_{2b1} dW - \int_{2c1} dW \neq 0 \quad (6.6)$$

Therefore,

$$\int_{2b1} dQ \neq \int_{2c1} dQ \quad (6.7)$$

Energy transfer as heat is not a point function, neither is it a property of the system.

Heat interaction is a path function.

Energy is a Property of the System

Refer to Figure 6.2 again and consider Eq. (6.5)

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

$$\int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW) \quad (6.8)$$

$\int dQ$ and $\int dW$ depend on path function followed by the system. The quantity $\int (dQ - dW)$ is the same for both the processes $2b1$ and $2c1$ connecting the states 2 and 1. The quantity $\int (dQ - dW)$ does not depend on path followed by the system, depends on the initial and final states. Hence $\int (dQ - dW)$ is an exact differential.

Differential of property of the system

This property is the internal energy of system, E

$$dU = dQ - dW \quad (6.9)$$

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 $dQ = 0, dW = 0$

$$dU = 0 \quad \text{or,} \quad U_2 = U_1 \quad (6.10)$$

A Perpetual Motion Machine of First Kind

Thermodynamics originated as a result of man's endeavour to convert the disorganized form of energy (internal energy) into organized form of energy (work).

$$\oint (dQ - dW) = 0 \quad \text{or,} \quad Q = W \quad (6.11)$$

An imaginary device which would produce work continuously without absorbing any energy from its surroundings is called a **Perpetual Motion Machine of the First kind**, (PMMFK). A PMMFK is a device which violates the first law of thermodynamics. It is impossible to devise a PMMFK (Figure 6.3)

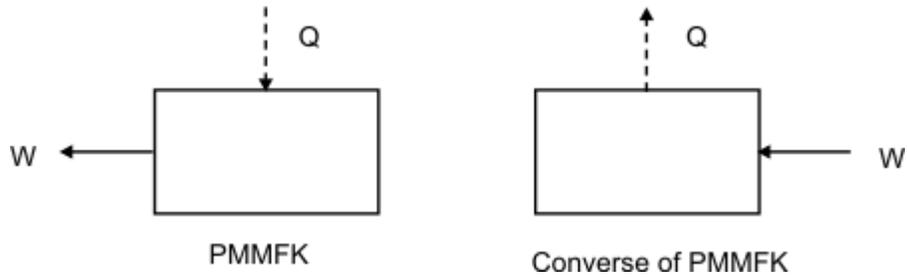


Figure 6.3

The converse of the above statement is also true, i.e., there can be no machine which would continuously consume work without some other form of energy appearing simultaneously.

Analysis of Closed System

Let us consider a system that refers to a definite quantity of matter which remains constant while the system undergoes a change of state. We shall discuss the following elementary processes involving the closed systems.

Constant Volume Process

Our system is a gas confined in a rigid container of volume V (Refer to Figure 6.4)

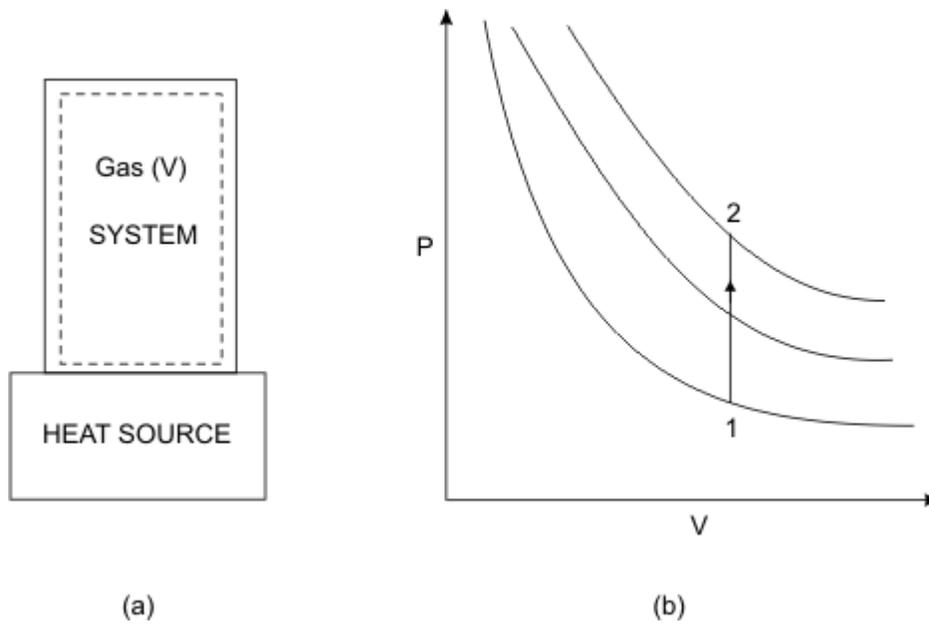


Figure 6.4

- Let the system be brought into contact with a heat source.
- The energy is exchanged reversibly. The expansion work done (PdV) by the system is zero.
- Applying the first law of thermodynamics, we get

$$dU = dQ \quad (6.12)$$

or,

$$Q = U_2 - U_1 \quad (6.13)$$

- Hence the heat interaction is equal to the change in the internal energy of the system.

Constant Volume Adiabatic Process

Refer to Figure 6.5 where a change in the state of the system is brought about by performing paddle wheel work on the system.

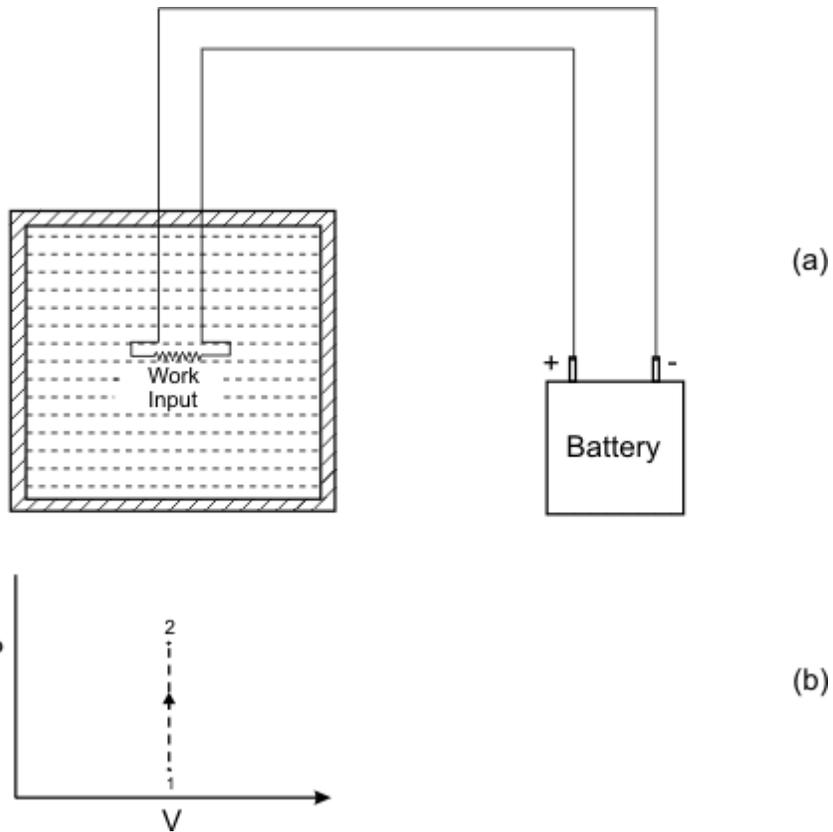


Figure 6.5

The process is irreversible. However, the first law gives

$$dU = -dW \quad (6.14)$$

or

$$-W = U_2 - U_1 \quad (6.14)$$

Interaction of heat and irreversible work with the system is same in nature. $(-W)$ represents the work done on the system by the surroundings

Specific Heat at Constant Volume

By definition it is the amount of energy required to change the temperature of a unit mass of the substance by one degree.

$$c_v = \left(\frac{dq}{dT} \right)_v \quad (6.16)$$

While the volume is held constant. For a constant volume process, first law of thermodynamics gives

$$dU = dQ \text{ or, } du = dq \quad (6.17)$$

Therefore,

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \quad (6.18)$$

Where u is the specific internal energy of the system. If c_v varies with temperature, one can use mean specific heat at constant volume

$$\bar{c}_v = \left[\int_{T_1}^{T_2} c_v dT \right] / (T_2 - T_1) \quad (6.19)$$

The total quantity of energy transferred during a constant volume process when the system temperature changes from T_1 to T_2

$$Q = m \int_{T_1}^{T_2} c_v dT = U_2 - U_1 \quad (6.20)$$

The unit for c_v is kJ/kgK. The unit of molar specific heat is kJ/kmolK.

Lecture 7 :

The lecture deals with

- Constant Pressure Process 1
- Constant Pressure Process 2
- Specific Heat at Constant Pressure
- Constant Temperature Process
- Adiabatic Process

Constant Pressure Process-1

A gas in the piston-cylinder assembly is considered as the system of interest (figure 7.1)

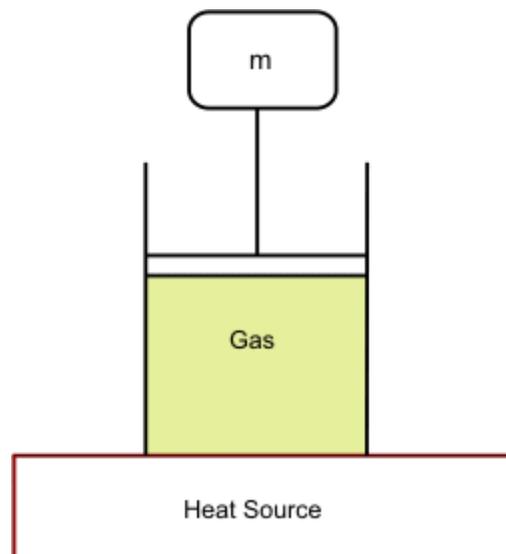


Figure 7.1

- The pressure is maintained at a constant value by loading the system with a mass.
- The cylinder is brought into contact with a heat source.

Energy transfer as heat takes place reversibly. The work is done by system when it changes from the initial state (1) to the final state (2).

$$W = \int_1^2 P dV = P(V_2 - V_1) \quad (7.1)$$

Applying the first law, we get

$$dU = dQ - dW = dQ - PdV = dQ - d(PV) \quad (7.2)$$

or

$$dQ = dU + d(PV) = d(U + PV) \quad (7.3)$$

or

$$dQ = dH \quad \text{or,} \quad Q = H_2 - H_1 \quad (7.4)$$

The quantity $(U + PV)$ is known as enthalpy, H (a property) of the system. The specific enthalpy h is defined as

$$h = H / m = u + Pv \quad (7.5)$$

The molar enthalpy is $\hat{h} = H / N$, where N is the mole number of the substance.

Constant Pressure Process-2

Let us assume paddle wheel work is done on the system figure 7.2. Also, consider adiabatic walls, so that

$$dQ = 0$$

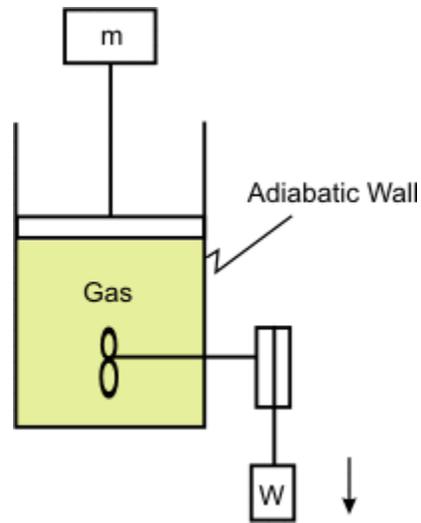


Figure 7.2

Now the application of first law enables us to write

$$dU = dQ - dW = dQ - (PdV + W_{sh}) \quad (7.6)$$

or

$$-dW_{sh} = dU + PdV = d(U + PV) = dH \quad (7.7)$$

or

$$-W_{sh} = H_2 - H_1 \quad (7.8)$$

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

Specific Heat at Constant Pressure

Let us focus on Figure 7.3

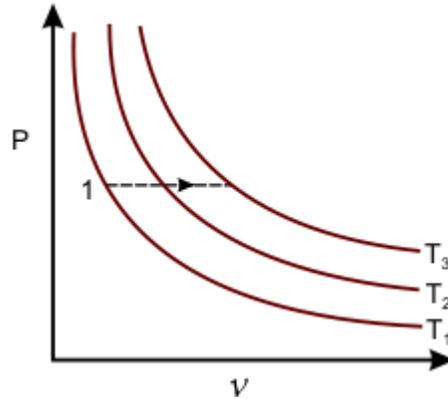


Figure 7.3

- System changes its state from 1 to 2 following a constant pressure process.
- There will be an accompanying change in temperature.

Specific heat at constant pressure is defined as the quantity of energy required to change the temperature of a unit mass of the substance by one degree during a constant pressure process.

$$c_p = \left(\frac{dq}{dT} \right)_p = \left(\frac{\partial h}{\partial T} \right)_p \quad (7.9)$$

The total heat interaction for a change in temperature from T₁ to T₂ can be calculated from

$$Q = m \int_{T_1}^{T_2} c_p dT = H_2 - H_1 \quad (7.10)$$

The molar specific heat at constant pressure can be defined as

$$\hat{c}_p = \left(\frac{\partial \hat{h}}{\partial T} \right)_p \quad (7.11)$$

Constant Temperature process

Let us refer to figure 7.4

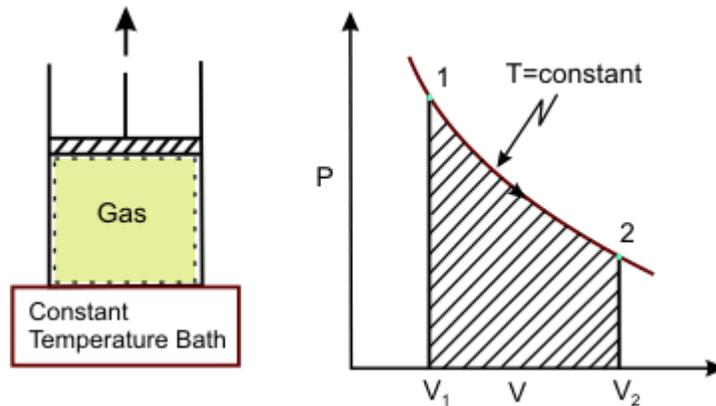


Figure 7.4

The system is allowed to undergo an expansion process while in contact with constant temperature bath. During the expansion process, the opposing force is continuously reduced. System is in equilibrium at all times. Applying the first law, one can write

$$dU = dQ - dW = dQ - PdV \quad (7.12)$$

For an ideal gas, the desired property relations are

$$Pv = RT \quad \text{and} \quad u = u(T) \quad (7.13)$$

Since the temperature is held constant, $du=0$ and $Q=W$. We can also write

$$q = w = \int_1^2 PdV = \int_1^2 \frac{RT}{v} dv = RT \ln \frac{v_2}{v_1}$$

Adiabatic Process

1. Irreversible Adiabatic Process

A process in which there is no energy transfer as heat across the boundaries of the system, is called an adiabatic process. For an adiabatic process, $Q=0$. Paddle wheel work is performed on the system (Figure 7.5).

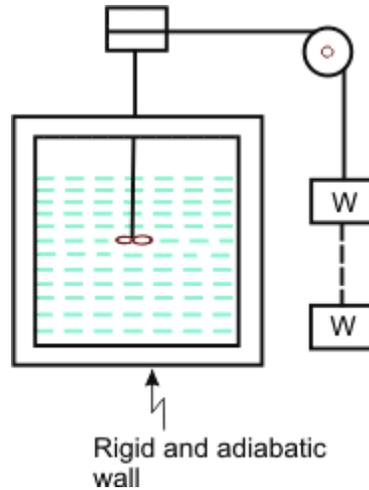


Figure 7.5

Application of first law gives

$$dU = dQ - dW = dQ - (W) = -dW \quad (7.15)$$

or

$$\Delta U = -W \quad (7.16)$$

2. Reversible Adiabatic (ISENTROPIC) Process

Consider a gas contained in the cylinder piston assembly as the system. The cylinder wall and the piston act as adiabatic walls. Suppose the gas is allowed to expand from the initial pressure P_1 to the final pressure P_2 and the opposing pressure is so adjusted that it is equal to inside gas pressure. For such a process, $dW = PdV$

The first-law of thermodynamics will give

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

Let us consider the system as an ideal gas which satisfies the relation $Pv = RT$ and $u = u(T)$. Also, we know that $du = c_v dT$.

or

$$du = -Pdv \quad (7.17)$$

or,

$$c_v(T_2 - T_1) = -\int Pdv \quad (7.18)$$

or

$$c_v(T_1 - T_2) = \int Pdv = w \quad (7.19)$$

or

For an ideal gas, $h = u + Pv = u + RT$

Therefore,

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p = c_v + R \quad (7.20)$$

The ratio of specific heats is given by

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{R}{c_v} \quad (7.21)$$

or,

$$c_v = \frac{R}{(\gamma - 1)} \quad (7.22)$$

Thus,

$$w = c_v(T_1 - T_2) = \frac{R(T_1 - T_2)}{(\gamma - 1)} = \frac{P_1 v_1 - P_2 v_2}{(\gamma - 1)} \quad (7.23)$$

Therefore when an ideal gas expands reversibly and adiabatically from the initial state (P_1, v_1, T_1) to final state (P_2, v_2, T_2) , the work done per mole of the gas is given by the above expression.

Lecture 8 :

The lecture contains

- Characterisation of Reversible Adiabatic Process
- Polytropic Process
- Ideal Gas Model

Characterisation of Reversible Adiabatic Process

Let us find out the path followed by the system in reaching the final state starting from the initial state. We have already seen that for an ideal gas

$$c_v dT = -Pdv = -\frac{RT}{v} dv \quad (8.1)$$

or,

$$\frac{dT}{T} = -\frac{R}{c_v} \frac{dv}{v} = -(\gamma - 1) \frac{dv}{v} \quad (8.2)$$

or,

$$\ln \frac{T_2}{T_1} = -(\gamma - 1) \ln \frac{v_2}{v_1} \quad (8.3)$$

or,

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{\gamma - 1} \quad (8.4)$$

or

$$\frac{T_2 v_2^{\gamma-1}}{T_1 v_1^{\gamma-1}} = 1 \quad \text{or} \quad T v^{\gamma-1} = \text{constant} \quad (8.5)$$

Since, $P v = RT$

$$\frac{T_2}{T_1} = \frac{P_2 v_2}{P_1 v_1} \quad (8.6)$$

From (8.4) and (8.6) we get

$$\frac{P_2 v_2}{P_1 v_1} = \left(\frac{v_1}{v_2} \right)^{\gamma-1} \quad (8.7)$$

or,

$$\frac{P_2 v_2^{\gamma}}{P_1 v_1^{\gamma}} = 1 \quad (8.8)$$

or,

$$P v^{\gamma} = \text{constant} \quad (8.9)$$

Polytropic Process

Ideal gas undergoes a reversible-adiabatic process; the path followed by the system is given by

$$P v^{\gamma} = \text{constant} \quad (8.10)$$

and the work done per kg of gas

$$w = \frac{P_1 v_1 - P_2 v_2}{\gamma - 1} \quad (8.11)$$

To generalise,

$$Pv^n = \text{constant}; w = \frac{P_1 v_1 - P_2 v_2}{n - 1} \quad (8.12)$$

n is polytropic index (γ is the property of the system, also it indicates reversible-adiabatic process)

$n = 0$, constant pressure process	$w = P(v_2 - v_1)$
$n = 1$, constant temperature process	$w = q = RT \ln \frac{v_2}{v_1}$
$n = \gamma$, reversible adiabatic process	$w = \frac{P_1 v_1 - P_2 v_2}{\gamma - 1}$
$n = \infty$, constant volume process	$w = 0$

Ideal Gas Model

- For many gases, the ideal gas assumption is valid and the $P-v-T$ relationship can be simplified by using the ideal gas equation of state: $Pv = RT$
- For an ideal gas, it has been mentioned that the specific internal energy u is a function of temperature only, $u = u(T)$
- Accordingly, specific enthalpy is a function of temperature only, since $h(T) = u(T) + pv = u(T) + RT$
- Physically, a gas can be considered ideal only when the inter-molar forces are weak.

This usually happens in low pressure and high temperature ranges.

$$c_v = \frac{du}{dT}, \quad c_p = \frac{dh}{dT} = \frac{d(u + Pv)}{dT} = \frac{d(u + RT)}{dT} = c_v + R \quad (8.13)$$

$$c_p = c_v + R \quad (8.14)$$

- Specific heat ratio $\gamma = c_p / c_v$, $c_p = c_v + R$

$$c_p(T) = \frac{\gamma R}{\gamma - 1}, \quad c_v(T) = \frac{R}{\gamma - 1} \quad (8.15)$$

$$du = c_v(T) dT \quad (8.16)$$

or,

$$u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T) dT \quad (8.17)$$

or,

$$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T) dT \quad (8.18)$$

- In some cases, the temperature dependence of the specific heat can be written in polynomial form.
- Otherwise, ideal gas tables are also available. They are easier to use compared to the thermodynamic tables since temperature is the only parameter.

Lecture 9 : **Thermodynamic Properties of Fluids**

The lecture deals with

- Thermodynamic Properties of Fluids
- Pure substance
- Equations of State
- Ideal Gas

Thermodynamic Properties of fluids

Most useful properties:

- Properties like pressure, volume and temperature which can be measured directly. Also viscosity, thermal conductivity, density etc can be measured.
- Properties like internal energy, enthalpy etc. which cannot be measured directly

Pure Substance

A pure substance is one which consists of a single chemical species.

Concept of Phase

Substances can be found in different states of aggregation. Ice, water and steam are the three different physical states of the same species H_2O . Based on the physical states of aggregation the substances are generally classified into three states as

- a. Solid
- b. liquid

c. gas

The different states of aggregation in which a pure substance can exist, are called its phases. Mixtures also exist in different phases. For example, a mixture of alcohol and water can exist in both liquid and vapour phases. The chemical composition of the vapour phase is generally different from that of the liquid phase.

Generalizing the above observations, it can be said that a system which is uniform throughout both in chemical composition and physical state, is called a homogeneous substance or a phase.

All substances, -solids, liquids and gases, change their specific volume depending on the range of applied pressure and temperature.

When the changes in the specific volume is negligible as in the case of liquids and solids, the substance may be treated as incompressible.

The isothermal compressibility of a substance κ is defined as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

The coefficient of volume expansion of a substance (β) is defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Equations of State

Equations that relate the pressure, temperature and specific volume or molar volume of a substance. They predict the $P-v-T$ relationship of a gas reasonably well within selected regions.

Boyle's law:

$$v \propto \left(\frac{1}{P}\right) \text{ at constant pressure}$$

or,

$$Pv = \text{Constant at constant temperature}$$

Charles' Law:

$$v \propto T \text{ At constant pressure}$$

$$P \propto T \text{ At constant volume}$$

Boyle's law and Charles' law can be combined to yield

$$Pv = RT$$

Where R is the characteristic gas constant. If the specific volume v is substituted by the molar volume, \bar{v} then R is substituted by the universal gas constant, $\bar{R} = 8.314 \text{ kJ / kmol K}$. Again, it can be shown that for an ideal gas $u = u(T)$.

In summary, the Ideal gas equation:

$$Pv = RT \text{ where } R \text{ is the specific constant}$$

$R = \frac{\bar{R}}{M}$, where \bar{R} is the universal gas constant (8.314 kJ / k mole K) M is the molar mass, defined as the mass of one mole of a substance. We can also write $P\bar{v} = \bar{R}T$ where \bar{v} is the molar volume.

Example: $M = 28 \text{ kg / kmol}$ for nitrogen (since its molar mass is 28)

$M = 32 \text{ kg / kmol}$ for oxygen (O_2 with a molar mass of 32)

Note: Many gases such as air, oxygen can be treated as ideal gases. However, dense gases such as water vapor and refrigerant vapor should not be treated as ideal gas. Use property table instead.

deal Gas

The kinetic theory of gases model a gas as a collection of elastic particles. The statistical analysis of these with some assumptions results as the ideal gas law

- Most gases deviate from ideal gas in the vicinity of the critical point and saturated vapour line
- Most gases behaves like ideal gas at high temperature and low pressure regions.

Joules Experiment

Refer to figure 9.1

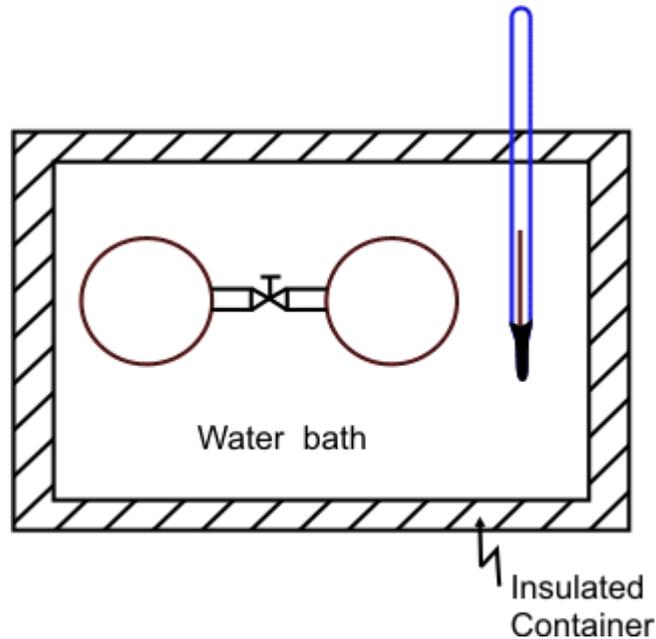


Figure 9.1

One of the vessels was filled in with air at 22 atm pressure and the other vessel was evacuated. The initial temperature of the water bath was measured. The valve was opened allowing air to occupy both the containers. The temperature of the water bath was measured again and it was found that the temperature did not change. The gas contained in both the vessels is our system. $W=0$ and $Q=0$. Since the number of moles of the gas also remains constant, it follows that $\Delta u = 0$. The pressure and the volume of the gas changed and yet the internal energy did not change. Hence

So,

$$\left(\frac{\partial u}{\partial P}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_T = 0 \quad (9.1)$$

$$u = u(T) \quad (9.2)$$

Since,

$$h = u + Pv = u + RT \quad (9.3)$$

$$h = h(T) \quad (9.4)$$

Van der Waal's equation of state:

The gases at low pressure and high temperatures follow ideal gas law. Gases that do not follow ideal gas law are required to be represented by a similar set of mathematical relations. The first effort was from Clausius.

Clausius Proposed

$$P(v-b) = RT \quad (9.5)$$

Van der Waals, by applying the laws of mechanics to individual molecules, introduced two correction terms in the equation of ideal gas. Van der Waals equation of state is given by.

$$\left(P + \frac{a}{v^2} \right) (v-b) = RT \quad (9.6)$$

The term (a/v^2) accounts for the intermolecular forces and b accounts for the volume occupied by the gas molecules.

Since Van der Waal's equation takes into account the inter-molecular forces, it is expected to hold good for liquid phase also. Now a days, the Van der Waal's equation is used to predict the phase equilibrium data. The constants a and b are determined from experimental $P-v-T$ data. However, rearranging the Van der Waal's equation, we get

$$P = \frac{RT}{(v-b)} - \frac{a}{v^2} \quad (9.7)$$

Therefore, a plot of P versus T at constant volume gives a straight line with a slope $R/(v-b)$ and an intercept $-(a/v^2)$. An interesting feature can be obtained from the following form

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0 \quad (9.8)$$

For low temperature, three positive real roots exist for a certain range of pressure. As the temperature increases, the three real roots approach one another and at the critical temperature they become equal.

For $T > T_c$ only one real value of v exists. $T < T_c$ three real values of v exists, where T_c is the critical temperature of the gas.

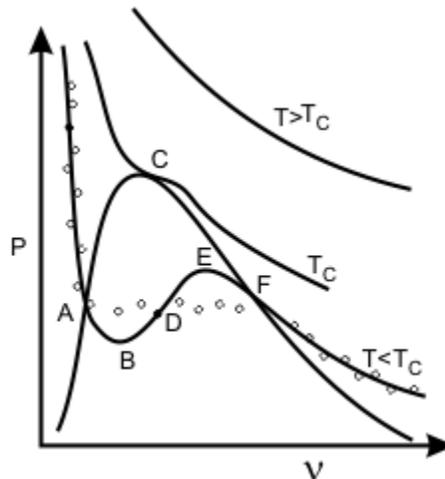


Figure 9.2

Refer to Fig 9.2. The curve ABDEF is predicted by the Van der Waals equation of state. The curve ABDEF is practically not realizable. The physically feasible curve is the straight line path from A to F. It can be shown that the straight line AF is such that the area ABDA is exactly equal to the area DEFD for a stable system.

Lecture 10 : The Constants of Van der Waals Equation and Compressibility Chart

The lecture deals with

- The Van der Waals Constants
- Virial Equation of State
- Compressibility Chart

The Van der Waals Constants

The constants a and b are different for different substances. We can get the estimates of a and b of a substance by knowing the critical values of that substance.

Before we proceed further, let us look at the mathematical function $f = f(x)$

For the maximum value of x : $\frac{df}{dx} = 0$ and $\frac{d^2f}{dx^2} < 0$

For the minimum value of x : $\frac{df}{dx} = 0$ and $\frac{d^2f}{dx^2} > 0$

For the point of inflection, $\frac{df}{dx} = 0$ and $\frac{d^2f}{dx^2} = 0$

From the Figure 9.2 we can see that the critical point is a point of inflection.

The critical isotherm must show a point of inflection at the critical point

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = \frac{-RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0 \quad (10.1)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0 \quad (10.2)$$

At the critical point, the Van der Waals equation is

$$\left(P_c + \frac{a}{v_c^2} \right) (v_c - b) = RT_c \quad (10.3)$$

One can solve the above three equations to obtain

$$v_c = 3b, T_c = \frac{8a}{27 Rb}, P_c = \frac{a}{27 b^2} \quad (10.4)$$

Alternatively, one can calculate the Van der Waals constants a and b in terms of critical constants.

$$a = \left(\frac{27 R^2 T_c^2}{64 P_c} \right), b = \left(\frac{RT_c}{8 P_c} \right) \quad (10.5)$$

The constants a and b can be determined for any substance from the critical point data (Table 10-1) At the critical point, one can see that

$$\frac{P_c v_c}{R T_c} = \frac{3}{8} = 0.375 \quad (10.6)$$

Table 10.1 Some typical values of Van der Waals constants

Gas	Constants a kPa (m ³ / kmol) ²	Constants b (m ³ / kmol)
Air	135.8	0.0364
Ammonia (NH ₃)	423.3	0.0373
Carbon-dioxide(CO ₂)	364.3	0.0427

Hydrogen (H ₂)	24.7	0.0265
Oxygen (O ₂)	136.9	0.0315
Nirtogen (N ₂)	136.1	0.0385
<i>P is in kPa, \bar{v} is in m³ / k mol, T is in K, R = 8.314 kJ / k mol K</i>		

Virial Equations of State

For any gas, we can write

$$(P\bar{v}) = RT \text{ as } P \rightarrow 0 \quad (10.7)$$

or,

$$\frac{P\bar{v}}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (10.8)$$

An alternate expression is

$$\frac{P\bar{v}}{RT} = 1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \dots \quad (10.9)$$

Both expressions are known as virial expansions introduced by Kamerlingh Onnes.

B', C', B, C etc are called virial coefficients. B' and B are called second virial coefficients, C' and C are called third virial coefficients and so on. For a given gas, these coefficients are functions of temperature only.

Compressibility Chart

To quantify deviation of real behavior from the ideal gas behavior, we introduce a new term namely, the compressibility factor. The compressibility factor Z is defined as the ratio of the actual volume to the volume predicted by the ideal gas law at a given temperature and pressure.

$Z = (\text{Actual volume}) / (\text{volume predicted by the ideal gas law})$

$$Z = \frac{v}{(RT/P)} = \frac{Pv}{RT} \quad (10.10)$$

If the gas behaves like an ideal gas, $Z=1$ at all temperatures and pressures. A plot of Z as a function of temperature and pressure should reveal the extent of deviation from the ideal gas law. Figure 10.1 shows a plot of Z as a function of temperature and pressure for N_2 .

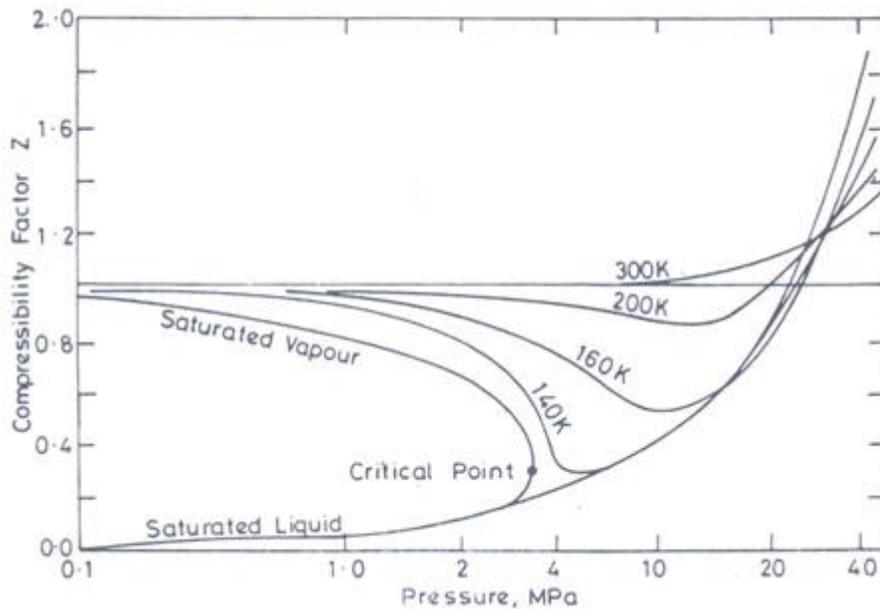


Figure 10.1

For each substance, a compressibility factor chart or compressibility chart is available.

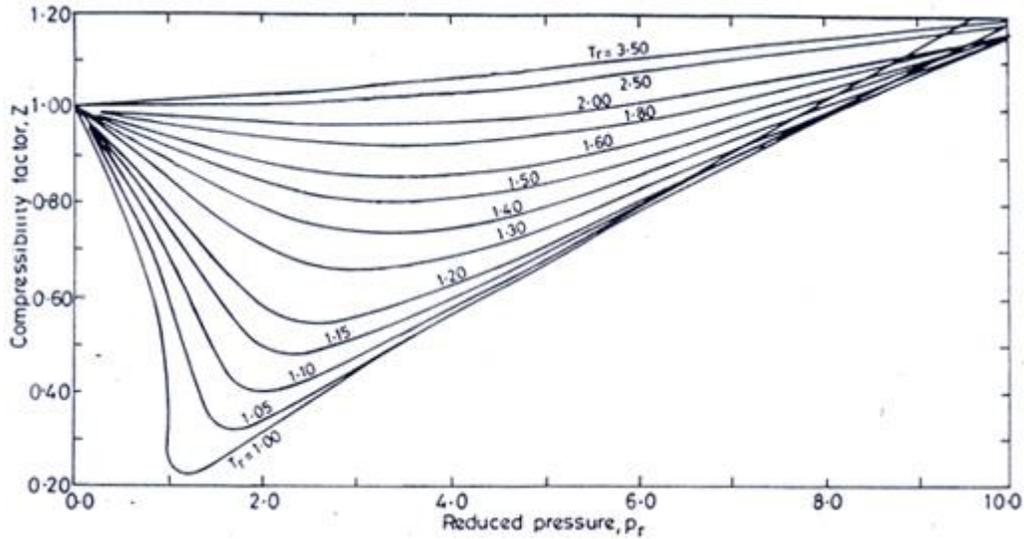


Figure 10.2

It would be very convenient if one chart could be used for all substances. The general shapes of the vapour dome and of the constant temperature lines on the $P-v$ plane are similar.

This similarity can be exploited by using dimensionless properties called reduced properties. The reduced pressure is the ratio of the existing pressure to the critical pressure of the substance and the same is followed for the reduced temperature and reduced volume. Then

$$P_r = P/P_c, T_r = T/T_c \text{ and } v_r = v/v_c \quad (10.11)$$

At the same temperature and pressure, the molar volumes of different gases are different. However, it is found from experimental data that at the same reduced pressure and reduced temperature, the reduced volumes of different gases are approximately the same.

Therefore for all substances

$$v_r = f(P_r, T_r) \quad (10.12)$$

or,

$$v_r = \frac{v}{v_c} = \frac{Z RTP_c}{Z_c RT_c P} = \frac{Z}{Z_c} \frac{T_r}{P_r} \quad (10.13)$$

Where $Z_c = (P_c v_c) / RT_c$. Z_c is called critical compressibility factor. Experimental values of Z_c for most substance fall with in a narrow range 0.2-0.3. Therefore from the above equation we can write

$$Z = f(P_r, T_r) \quad (10.14)$$

When Z is plotted as a function of reduced pressure and T_r , a single plot, known as general compressibility chart (Figure 10.2) is found to be satisfactory for a wide variety of substances. Although necessarily approximate, the plots are extremely useful in situations where detailed data on a particular gas are lacking but its critical properties are available.

Lecture 11 : Phase-Change Process of Pure Substances

The lecture deals with

- Graphical Representation of $P-v-T$ Data for Pure Substances
- Specific internal energy and enthalpy
- Steam Tables

There are certain situations when two phases of a pure substance coexist in equilibrium. As a commonly used substance water may be taken up to demonstrate the basic principles involved. However, all pure substances exhibit the same general behaviour.

We shall remember the following definitions:

Saturated State: A state at which a phase change begins or ends

Saturation Temperature: Temperature at which phase change (liquid-vapour) begins or ends at a given pressure

$$T_{sat} = T_{sat} (P)$$

Saturation Pressure: It is the pressure at which phase change begins or ends at a specified temperature.

$$P_{sat} = P_{sat} (T)$$

Saturated Liquid: It is the substance at T_{sat} which is fully liquid (no-vapour).

Saturated Vapour: It is the substance at T_{sat} which is fully vapour (no-liquid).

Subcooled liquid: If the temperature of the liquid (T) is less than T_{sat} then the liquid is called sub-cooled liquid.

Superheated vapour: If the temperature of the vapour (T) is greater than T_{sat} then the vapour is called superheated vapour.

Graphical Representation of $P-v-T$ Data for Pure Substances

The commonly used thermodynamic diagrams are

- a. Pressure versus Temperature (P – T)
- b. Pressure versus Volume (P – v)
- c. Temperature versus Volume (T – v)

- d. Temperature versus entropy ($T - S$)
- e. Enthalpy versus entropy ($h - S$)
- f. Pressure versus enthalpy ($P - h$)

(a) Pressure-Temperature Diagram

For water , at 100 kPa, the saturation temperature is 99.6°C. Alternatively at 99.6°C, the saturation pressure is 100 kPa. Quite often, the saturation pressure is called the vapour pressure.

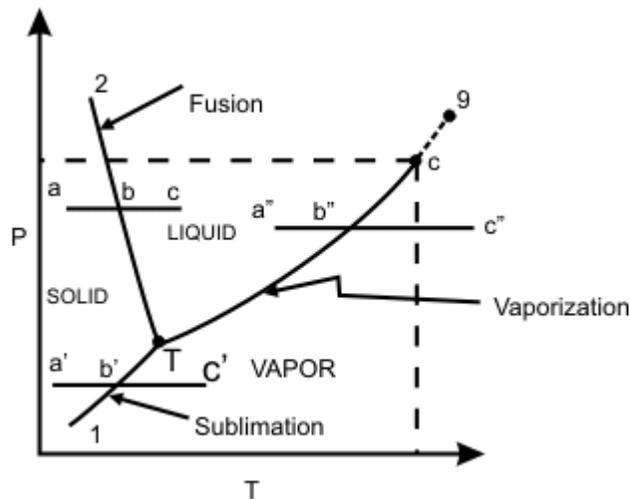


Figure 11.1

Refer to figure 11.1, The segment 1-T represents sublimation process during which solid and vapour phases coexist in equilibrium. The segment 2-T represents fusion process during which solid and liquid phases coexist in equilibrium. The segment T-C represents vapourization .

Sublimation curve 1-T separates solid and vapour. 2-T separates solid and liquid and T-C separates liquid and vapour. Three curves meet at T, which is called **the triple-point**, where all the three phases-solid, liquid and vapour coexist in equilibrium. At the triple point no thermodynamic property of the system can be varied independently. The system is said to be invariant.

Along, 1-T, or T-C, the system is univariant, that is only one thermodynamic property of the system can be varied independently. The system is bivariant in the single phases region.

The curve 2-T can be extended indefinitely, the curve T-C terminates at point C which is called the **critical point**.

The **critical point** represents highest temperature and pressure at which both the **liquid phase** and **vapour phase** can coexist in **equilibrium**.

At the **critical point**, the **specific volumes** and all other **thermodynamic** properties of the liquid phase and the vapour phase are identical.

T_c and P_c are called the critical temperature and critical pressure, respectively. If the substance exist as a liquid on the curve T-C, it is called **saturated liquid**, and if it exists as a vapour, it is called a **saturated vapour**. Under the constant pressure, the line abc indicates melting, $a'b'c'$ - sublimation and $a''b''c''$ - vaporization.

(b) $P-v$ Diagram

Refer to the $P-v$ diagram as shown in Figure 11.2.

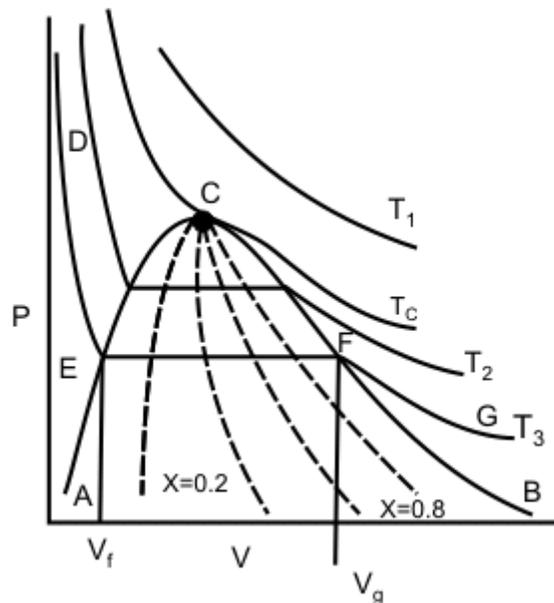


Figure 11.2

The isotherm T_1 is at a temperature greater than the critical temperature T_c . The isotherms T_2 and T_3 are at temperatures less than the critical temperature and they cross the phase boundary. The point C represents the critical point. The curve AC is called the saturated liquid line; and the curve CB is called the saturated vapour line. The area under the curve ACB is the two-phase region where both liquid and vapour phase are present. Left to the curve AC is the liquid region. Region to the right of curve CB is the vapour region

The isotherm T_3 appears in three segments: DE, EF and FG. DE is almost vertical, because the change in the volume of liquid is very small for a large change in pressure. The segment FG is less steep because vapour is compressible. Segment EF is horizontal, because the phase change from liquid to vapour occurs at constant pressure and constant temperature for a pure substance. EF represents all possible mixtures of saturated liquid and saturated vapour. The total volume of the mixture is the sum of the volumes of the liquid and vapour phases.

$$V = V_{liq} + V_{vap} \quad (11.1)$$

Dividing by the total mass m of the mixture, an average specific volume for mixture is obtained

$$v = \frac{V}{m} = \frac{V_{liq}}{m} + \frac{V_{vap}}{m} \quad (11.2)$$

Since the liquid phase is a saturated liquid and the vapour phase is a saturated vapour,

$$V_{liq} = m_{liq} v_f \quad \text{and} \quad V_{vap} = m_{vap} v_g \quad (11.3)$$

so,

$$v = \frac{m_{liq}}{m} v_f + \frac{m_{vap}}{m} v_g \quad (11.4)$$

Introducing the definition of quality or dryness fraction $X = m_{vap} / m$ and noting that $m_{liq} / m = 1 - X$, the above expression becomes

$$v = (1 - X) v_f + X v_g \quad (11.5)$$

The increase in specific volume due to vaporization $(v_g - v_f)$ is often denoted by v_{fg}

$$v = v_f + X v_{fg} \quad (11.6)$$

Again we can write

$$m v = (m_{liq} + m_{vap}) v = m_{liq} v_f + m_{vap} v_g \quad (11.7)$$

or,

$$m_{liq} (v - v_f) = m_{vap} (v_g - v) \quad (11.8)$$

or,

$$\frac{m_{liq}}{m_{vap}} = \frac{(v_g - v)}{(v - v_f)} \quad (11.9)$$

Known as lever rule. At the critical point, the specific volumes and all other thermodynamic properties of the liquid phase and the vapour phase are identical.

(c) $T - v$ Diagram

Refer to $T - v$ diagram shown in Fig 11.3. Let us consider constant pressure heating of liquid water in a cylinder-piston assembly. If the water is initially at state 1, on heating at constant pressure, the temperature and the specific volume of the water increase and follows the path 1-2 as shown in Fig 11.3(a).

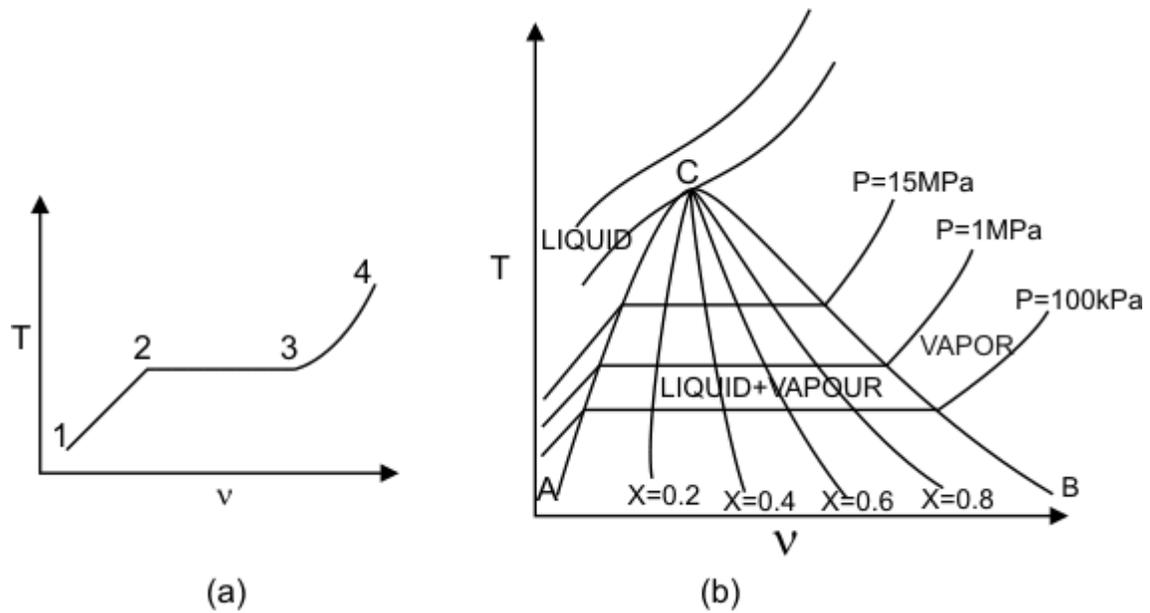


Figure 11.3

At point 2 vaporization starts. The vaporization process is represented by 2-3. During vaporization, temperature and pressure remain constant. The point 3 represents saturated vapour. Further heating produces super heated vapour, that is vapour above its saturation temperature at the specified pressure. If the constant pressure heating is done at several different pressures, the resulting temperature-volume diagram becomes as it is shown in Fig 11.3 (b). The curve AC represents saturated liquid line and the curve BC represents the saturated vapour line.

(d) T-s diagram

Let us refer to the T-s diagram shown in Figure 11.4

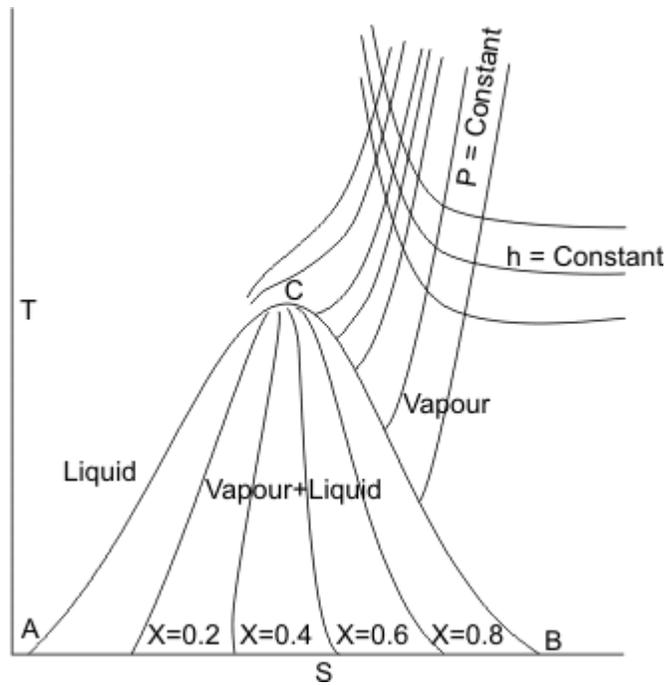
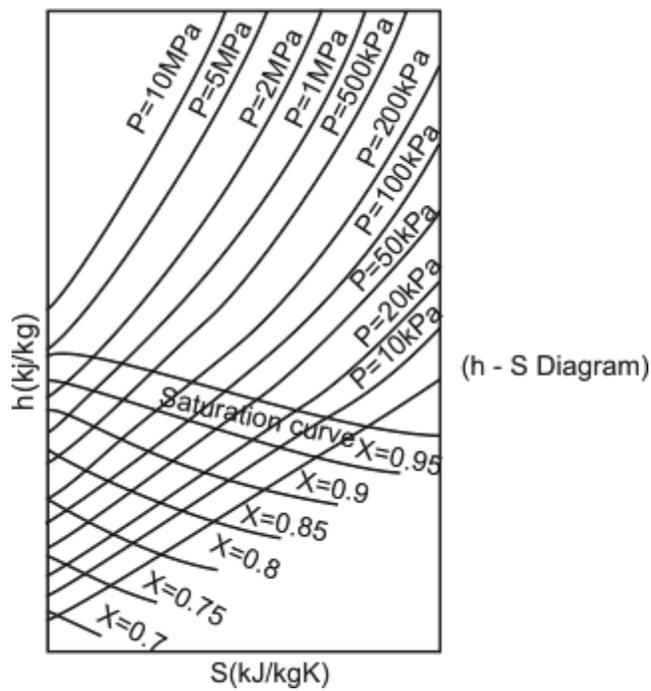


Figure 11.4

(e) Enthalpy-entropy diagram or Mollier diagram.

Refer to figure 11.5 which is known as h-s diagram.



- Heat interaction in an isobaric process is equal to change in enthalpy of the system.
- For a flow process (will be discussed later) the work done by an adiabatic device is equal to the decrease in enthalpy of the flowing fluid.
- A throttling process is an isenthalpic process. A throttling process is a process in which a fluid flows from a region of high pressure to a region of low pressure without exchanging energy as heat or work.
- A reversible adiabatic process is an isentropic process.

Specific internal energy and enthalpy

$$H = PV + U$$

or,

$$h = u + P\nu \text{ [on a unit mass basis]}$$

or,

$$\hat{h} = \hat{u} + P\hat{\nu} \text{ [on per mole basis]}$$

Data for specific internal energy, u and enthalpy, h can be calculated from the property tables in the same way as for specific volume.

$$u = (1 - X)u_f + Xu_g = u_f + X(u_g - u_f) \quad (11.10)$$

Increase in specific internal energy $(u_g - u_f)$ is often denoted by u_{fg} . The specific enthalpy is

$$h = (1 - X)h_f + X h_g + X(h_g - h_f) \quad (11.11)$$

Increase in specific enthalpy $(h_g - h_f)$, is often denoted by h_{fg} .

Steam Tables

Two Saturated steam tables

- Saturated Steam Pressure Table
- Saturated Steam Temperature Table

Similar tables can exist for any pure substance (e.g. Freon 12)

Saturated Steam: Pressure Table (kJ/kg)

P (bar)	T (°C)	ν (m ³ /kg)		h (kJ/kg)		s (kJ/kg k)	
		ν_f	ν_g	h_f	h_g	s_f	s_g
0.01	6.98						
0.05	32.90						
0.10	45.83						
.	.						
.	.						
.	.						
2.0	120.23						

In this table pressure is selected as the independent variable.

Saturated Steam: Temperature Table

T (°C)	P (bar)	ν		h		s	
		ν_f	ν_g	h_f	h_g	s_f	s_g
0	6.1×10^{-3}						

2							
4							
.	.						
.	.						
.	.						
374.15	221.2						

Superheated Steam Table

P(bar) (0.2)			Temperature (°C)			
T_{sat} (60.09)		100	200	300	400	
	v (m ³ /kg)	8.5				
	h (kJ/kg)	2686				
	s (kJ/kg k)	8.126				

The values for a given condition are to be evaluated through interpolation.

Lecture 12 : First Law of Thermodynamics for a Continuous System

The lecture deals with

- Conservation of Mass applied to a control volume
- Conservation of Energy applied to a Control Volume

Conservation of Mass applied to a control volume

Let us consider the law of conservation of mass as applied to the control volume.

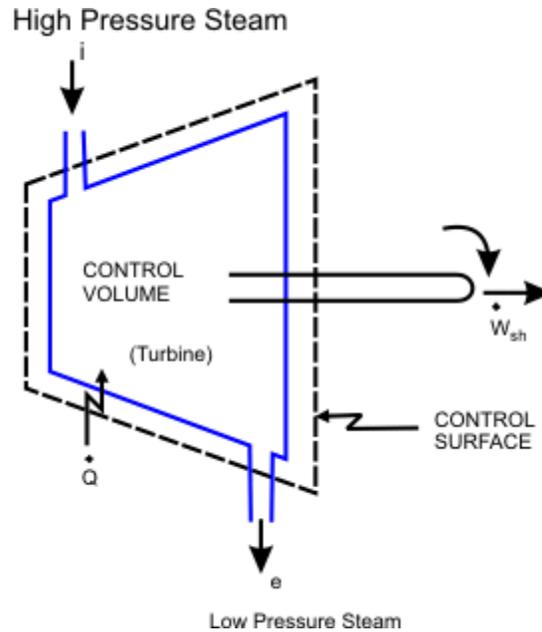


Figure 12.1

During a time interval dt , let the mass dm_i enter the control volume and the mass dm_e leave the control volume. Let $m(t)$ represent the mass inside the control volume at time t , and $m(t+dt)$ represent the mass inside the control volume at time $(t+dt)$. The law of conservation of mass gives:

$$m(t+dt) = m(t) + dm_i - dm_e \quad (12.1)$$

$$m(t+dt) - m(t) = dm_i - dm_e \quad (12.2)$$

Here the LHS gives the change in mass within the CV during the time interval dt , while RHS gives the net mass flow into the CV during the time dt . Dividing both sides of the equation by dt , we get

$$\frac{[m(t+dt) - m(t)]}{dt} = \frac{dm_i}{dt} - \frac{dm_e}{dt} \quad (12.3)$$

In the limiting case as $dt \rightarrow 0$, we obtain

$$\frac{dm}{dt} = \dot{m}_i - \dot{m}_e \quad (12.4)$$

The LHS gives rate of accumulation of mass inside the CV and the RHS has respective terms giving rate of mass entering the CV and rate of mass leaving the CV.

If the CV has many inlet and exit ports, the equation becomes

$$\frac{dm}{dt} = \sum \dot{m}_i - \sum \dot{m}_e \quad (12.5)$$

(b) Conservation of Energy applied to a Control Volume

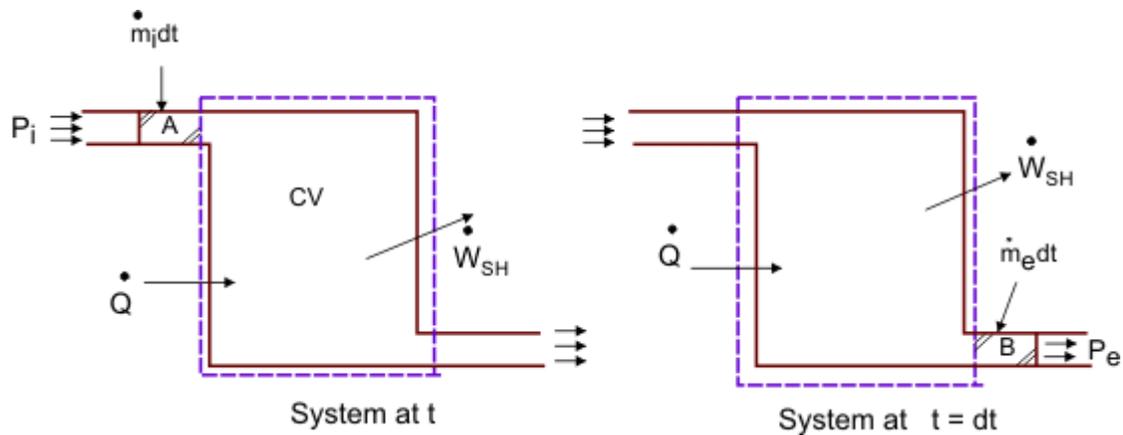


Figure 12.2

Let $m(t)$ = total mass inside the CV at time t .

$m(t + dt)$ = total mass inside the CV at time $t + dt$.

$e(t) = (u + V^2 / 2 + gZ)$ = specific energy of matter inside the control volume at time t .

$e(t + dt)$ = specific energy of matter inside the control volume at time $t + dt$.

P_i and P_e = Pressure at the inlet and exit ports, respectively.

V_i and V_e = Flow velocity at the inlet and exit ports, respectively.

v_i and v_e = specific volumes at the inlet and exit ports respectively

e_i and e_e = specific energy of the material at the inlet and exit ports respectively.

\dot{Q} = Rate of energy flow as heat into the control volume

\dot{W}_{sh} = Rate of shaft work done by the control volume

The mass contained in the region A which enters the control volume during the time interval $dt = \dot{m}_i dt$

The mass contained in the region B which leaves the control volume during the time interval $dt = \dot{m}_e dt$

From the mass balance, we can write

$$m(t) + \dot{m}_i dt = m(t + dt) + \dot{m}_e dt \quad (12.6)$$

where $\dot{m}_i dt$ is the mass entering the control volume during the differential time dt . To accommodate this, the mass inside the control volume has to be compressed such that its volume decreases by the amount $\dot{m}_i v_i dt$. This is accomplished by the pressure P_i acting on the material entering the control volume. Therefore, the work done = $-P_i v_i \dot{m}_i dt$

Since the mass $\dot{m}_e dt$ has to leave the control volume at the exit port, the work done = $P_e v_e \dot{m}_e dt$,

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

Energy of the system at time $t + dt = m(t + dt)e(t + dt) + \dot{m}_e e_e dt = E(t + dt) + \dot{m}_e e_e dt$

During the time interval dt , We may account for the following

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

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

Energy flow as heat into the control volume and the shaft work delivered by the control volume are taken as positive. By applying the first law of thermodynamics, we get

$$(E_2 - E_1) = Q - W \quad (12.7)$$

or,

$$[E(t+dt) + \dot{m}_e e_e dt] - [E(t) + \dot{m}_i e_i dt] = \dot{Q} dt - \dot{W}_{sh} dt - (P_e v_e \dot{m}_e - P_i v_i \dot{m}_i) dt \quad (12.8)$$

or,

$$\dot{m}_e (e_e + P_e v_e) - \dot{m}_i (e_i + P_i v_i) = \dot{Q} - \dot{W}_{sh} - \frac{E(t+dt) - E(t)}{dt} \quad (12.9)$$

In the limiting case, $dt \rightarrow 0$

$$\dot{m}_e \left(h_e + \frac{V_e^2}{2} + gZ_e \right) - \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gZ_i \right) = \dot{Q} - \dot{W}_{sh} - \frac{dE}{dt} \quad (12.10)$$

Where,

$$h_e = u_e + P_e v_e \quad \text{and} \quad h_i = u_i + P_i v_i$$

Z_e, Z_i = elevation of the exit and inlet ports above the datum level. The above expression can now be rearranged as

$$\frac{dE}{dt} = \left[\dot{m}_i \left(h_i + \frac{V_i^2}{2} + gZ_i \right) + \dot{Q} \right] - \left[\dot{m}_e \left(h_e + \frac{V_e^2}{2} + gZ_e \right) + \dot{W}_{sh} \right] \quad (12.11)$$

Rate of energy accumulation = Rate of energy inflow - Rate of energy outflow

Lecture 13 : Steady-state Flow Processes

The lecture contains

- Steady State Flow Processes
- Application of Steady State Flow Processes

Steady-state Flow Processes

Many of the engineering devices like turbines, compressors, pumps, nozzles, condensers, heat exchangers etc. operate at steady state conditions. The general expression developed for the control volume in the earlier lecture can be simplified if steady flow conditions are assumed.

These are:

- The mass flows into the control volume at a constant rate and leaves the control volume at the same rate. Therefore, there is no accumulation of mass inside the control volume. Thus, $\dot{m}_i = \dot{m}_e = \dot{m}$.

or,

$$\frac{d}{dt} \int_V \rho dV = \frac{dm}{dt} = 0 \quad (13.1)$$

- The state of the matter at the inlet, exit and at any given point inside the control volume does not change with respect to time. Therefore,

$$\frac{d}{dt} \int_V \rho e dV = \frac{dE}{dt} = 0 \quad (13.2)$$

- The rate of energy transfer as heat and work across the control surface is a constant. $\dot{Q} = \text{constant}$; $\dot{W}_{sh} = \text{constant}$

With these, the first law for the control volume reduces to the form

$$\left(h_e + V_e^2 / 2 + gZ_e\right) - \left(h_i + V_i^2 / 2 + gZ_i\right) = \frac{(\dot{Q} - \dot{W}_{sh})}{\dot{m}} \quad (13.3)$$

Application of Steady-state Flow Processes

(a) Turbine:

Turbine converts enthalpy into useful work. Steam or gas at high temperature and pressure is allowed to expand through a system of rotors.

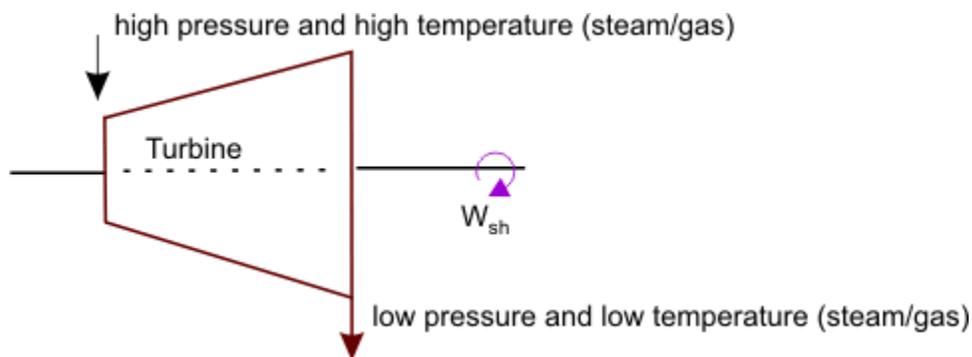


Figure 13.1

The change in kinetic and potential energy of steam or gas as it passes through the turbine can be ignored without introducing much error. Further, if the heat losses from the turbine are negligible, the first law for this steady state flow reduces to

$$h_e - h_i = -\dot{W}_{sh} / \dot{m} \quad (13.4)$$

Therefore, in an adiabatic turbine, the work done per unit mass of the fluid is equal to the decrease in the enthalpy of the fluid. Here, \dot{W}_{sh} is positive; $h_i > h_e$

(b) Compressor:

A compressor can be considered as a turbine operating in reverse. Fluid enters the

compressor at a low pressure and emanates at a higher pressure. If the changes in the kinetic energy and potential energy are ignored, and the energy losses are negligible, then the first law for this flow process reduces to

$$h_e - h_i = -\dot{W}_{sh} / \dot{m} \quad (13.5)$$

In a compressor, \dot{W}_{sh} is negative. Because the work is being done on the system, $h_e > h_i$. The work done on the compressor per unit mass of the fluid is equal to the increase in enthalpy of the fluid. The compressors discharge the fluid with higher enthalpy, i.e., with higher pressure and temperature.

(c) Nozzle:

A nozzle is primarily used to increase the flow velocity.

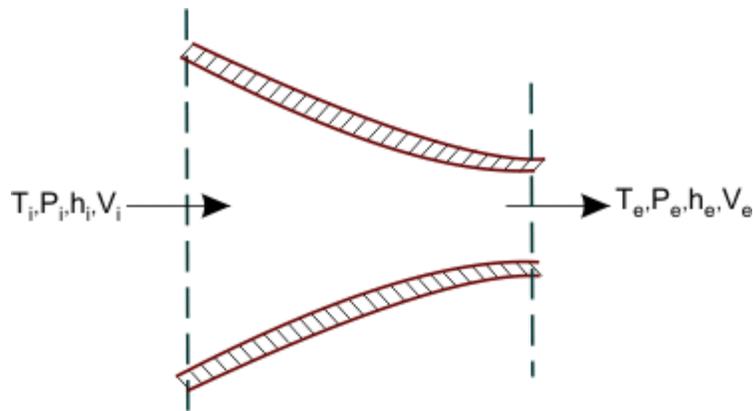


Figure 13.2

The first law reduces to

$$h_e + \frac{V_e^2}{2} = h_i + \frac{V_i^2}{2} \quad (13.6)$$

or,

$$V_e^2 - V_i^2 = 2(h_i - h_e) \quad (13.7)$$

If the inlet velocity is negligible $V_i \approx 0$, and then $V_e = \sqrt{2(h_i - h_e)}$ otherwise, $V_e = \sqrt{2(h_i - h_e) + V_i^2}$. The velocity is increased at the cost of drop in enthalpy. If an

ideal gas is flowing through the nozzle, the exit velocity V_e can be expressed in terms of inlet and outlet pressure and temperatures by making use of the relations: $Pv = RT$ and $dh = c_p dT$.

Therefore,

$$V_e^2 = 2c_p(T_i - T_e) = 2c_p T_i \left(1 - \frac{T_e}{T_i}\right) \quad (13.8)$$

From the relations governing adiabatic expansion,

$$\frac{T_e}{T_i} = \left(\frac{P_e}{P_i}\right)^{\frac{\gamma-1}{\gamma}} \quad (13.9)$$

We get,

$$V_e = \sqrt{2C_p T_i \left[1 - \left(\frac{P_e}{P_i}\right)^{\frac{\gamma-1}{\gamma}}\right]} \quad (13.10)$$

(d) Diffuser: A diffuser can be thought of as a nozzle in which the direction of flow is reversed.

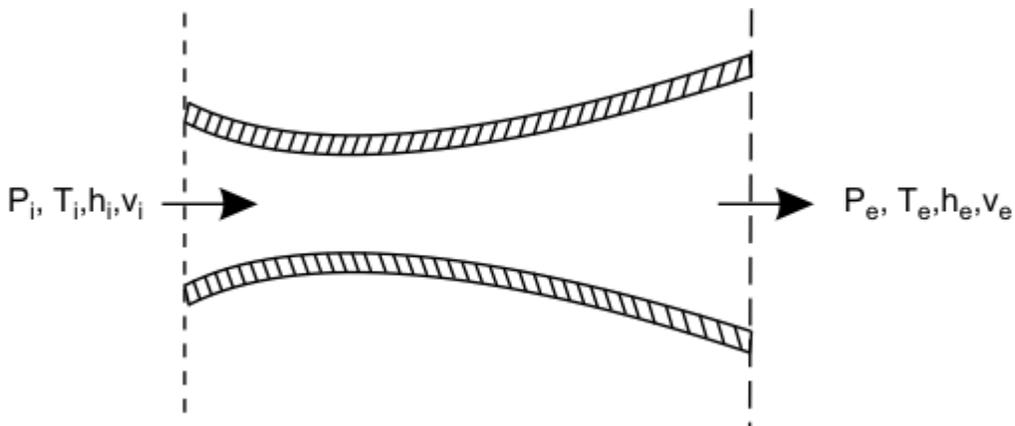


Figure 13.3

For an adiabatic diffuser, \dot{Q} and \dot{W}_{sh} are zero and the first law reduces to

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

$$V_e^2 - V_i^2 = 2(h_i - h_e) \quad (13.11)$$

The diffuser discharges fluid with higher enthalpy. The velocity of the fluid is reduced.

(e) Heat Exchangers

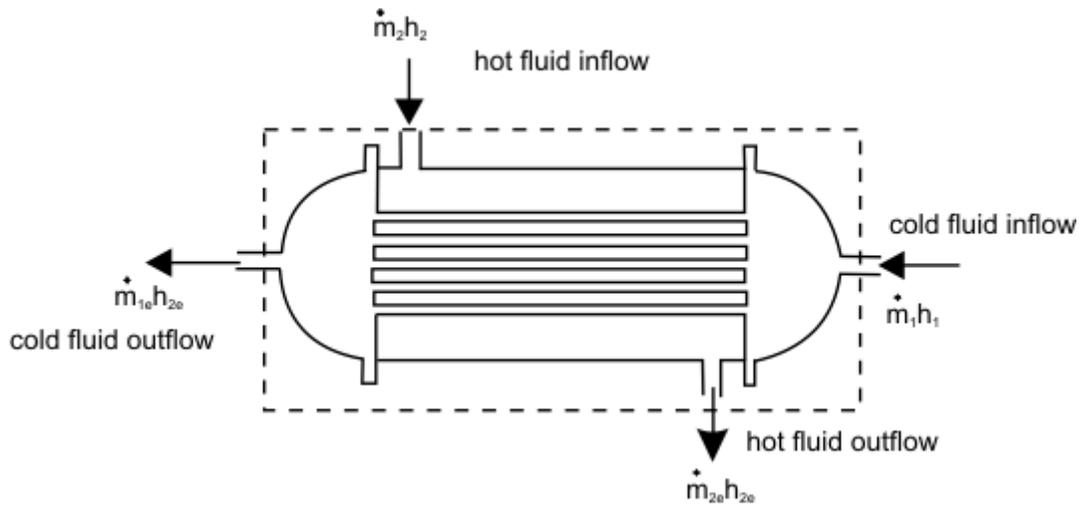


Figure 13.4

The figure 13.4 explains the working of a simple heat exchanger. The governing equation may be modified for multiple entry and multiple exit of the system as

$$\sum \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gZ_e \right) - \sum \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gZ_i \right) = \dot{Q} - \dot{W}_{sh} \quad (13.12)$$

$$\dot{W}_{sh} = 0, \quad \dot{Q} = 0, \quad \Delta \left(\frac{V^2}{2} \right) = 0, \quad \Delta(gZ) = 0 \quad (13.13)$$

$$\sum \dot{m}_e h_e = \sum \dot{m}_i h_i \quad (13.14)$$

$$\dot{m}_{1e} h_{1e} + \dot{m}_{2e} h_{2e} = \dot{m}_{2i} h_{2i} + \dot{m}_{1i} h_{1i} \quad (13.15)$$

Further, $\dot{m}_{1e} = \dot{m}_{1i} = \dot{m}_1$ and $\dot{m}_{2e} = \dot{m}_{2i} = \dot{m}_2$

$$\dot{m}_1 (h_e - h_i)_1 = \dot{m}_2 (h_i - h_e)_2 \quad (13.16)$$

\dot{m}_1 is the mass flow rate of cold fluid and \dot{m}_2 is the mass flow rate of hot fluid.

Lecture 14 : Throttling Process

The lecture contains

- Throttling Process
- Application of Throttling Process

Throttling Process:

The porous plug experiment was designed to measure temperature changes when a fluid flows steadily through a porous plug which is inserted in a thermally insulated, horizontal pipe. The apparatus used by Joule and Thomson is shown in Figure 14.1.

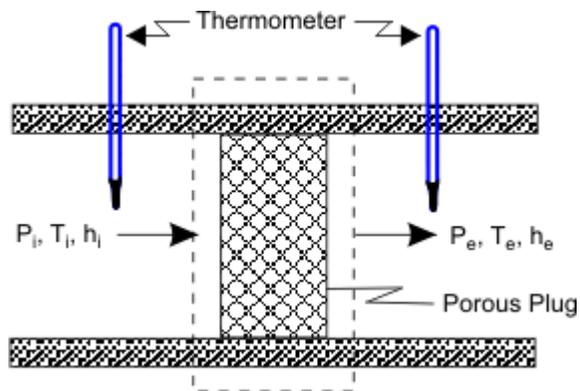


Figure 14.1

A gas at pressure P_i and temperature T_i flows continuously through a porous plug in a tube and emerges into a space which is maintained at a constant pressure P_e . The device is thermally insulated and kept horizontal. Consider the dotted portion as control volume.

$\dot{Q} = 0, W_{sh} = 0$. This results in $h_i = h_e$

Therefore, whenever a fluid expands from a region of high pressure to a region of low pressure through a porous plug, partially opened valve or some obstruction, without exchanging any energy as heat and work with the surrounding (neglecting the changes in PE and KE), the enthalpy of the fluid remains constant, and the fluid is said to have undergone a **throttling process**. If the downstream pressure is held at several different values successively and at each of these T_e is measured, we shall obtain a situation explained by Figure 14.2.

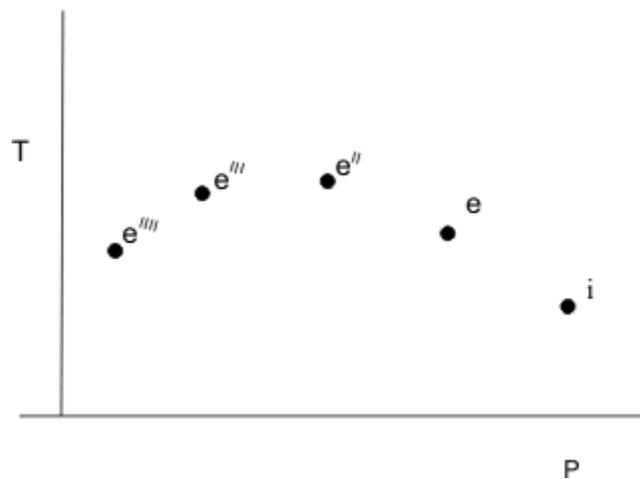


Figure 14.2

Each plotted point represents a state for which the enthalpy is equal to h_i . If we join all these points we shall be able to obtain a constant enthalpy line (figure 14.3).

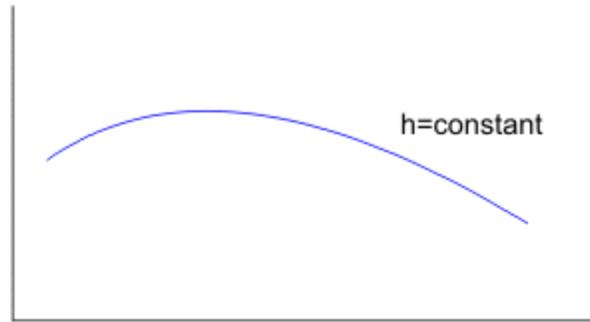


Figure 14.3

Such a plot of P versus T yields may also be called **isenthalpic curve**. The slope of the isenthalpic curve is called the Joule-Thomson coefficient and given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

The experiments are conducted with different P_i and T_i in order to find out the isenthalpic curves. A family of isenthalpic curves is shown in Figure 14.4 which is typical of all real gases.

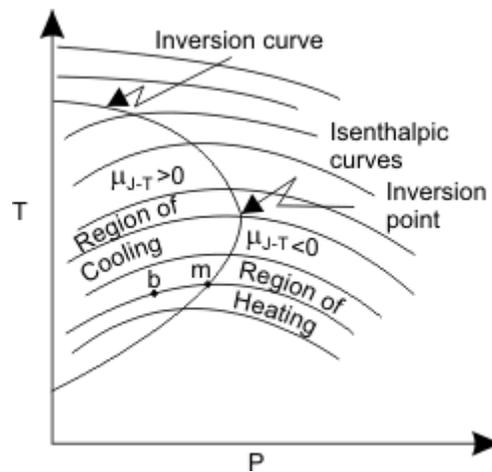


Figure 14.4

The point at which $\mu_{JT} = 0$ is called the **inversion point**. The locus of all the inversion points is the inversion curve.

In the region left of the inversion curve, $\mu_{JT} > 0$. In the throttling process the downstream pressure P_e is always less than the upstream pressure P_i . Therefore, whenever a real gas is subjected to throttling, the temperature of the gas decreases if the initial state lies in the region to the left of the isenthalpic curve. This is explained by a process from m to b in Figure 14.4.

To the right of the inversion curve, $\mu_{JT} < 0$. If the initial state of gas lies in the region to the right of the inversion curve, the temperature of the gas increases upon throttling. For almost all the gases, at ordinary range of pressures and temperature, $\mu_{JT} > 0$ and the maximum inversion temperature is above the room temperature. The exceptions are hydrogen, helium and neon. For hydrogen, the maximum inversion temperature is 200 K and for helium the maximum inversion temperature is 24 K. If hydrogen is throttled at room temperature, the temperature of the gas increases. To produce low temperature by throttling, the initial temperature of hydrogen should be below 200 K. This is usually accomplished by cooling with liquid nitrogen. Similarly, in the production of liquid helium by throttling, the initial temperature of helium should be below 24 K. Hence it is cooled by liquid hydrogen prior to throttling.

Suppose an ideal gas is throttled. Since throttling process is isenthalpic, and for an ideal gas enthalpy is a function of temperature only, the temperature of an ideal gas does not change during a throttling process. Hence $\mu_{JT} = 0$ for an ideal gas.

Applications of Throttling

(a) Refrigeration

The working fluid (called refrigerant) leaving the evaporator as vapour at state 1 undergoes an adiabatic compression in a compressor and leaves as saturated vapour at state 2. This compressed refrigerant enters a condenser where it rejects heat to the ambient atmosphere and leaves as a saturated liquid at high pressure at state 3. Then the liquid refrigerant at high pressure undergoes throttling and leaves as a mixture of liquid and vapour at low pressure at state 4. During throttling, the liquid vaporizes partially and its temperature decreases. The cooled refrigerant then passes through an evaporator where it absorbs energy from the body to be cooled, and leaves as hot vapor at state 1. Finally, the hot refrigerant vapour goes to the compressor, thus completing a cycle.

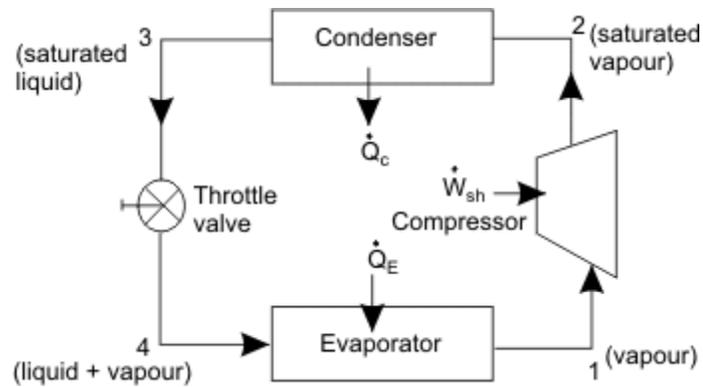


Figure 14.5

Applying the first law of thermodynamics to each of the units (control volume) the following relations are obtained:

Compressor (adiabatic) $h_2 - h_1 = -\dot{W}_{sh} / \dot{m}$

Condenser (constant pressure cooling) $h_3 - h_2 = -\dot{Q}_c / \dot{m}$

Throttling (isenthalpic) $h_4 - h_3 = 0$

Evaporator (constant pressure heat addition) $h_1 - h_4 = \dot{Q}_E / \dot{m}$

The coefficient of performance (COP) of the refrigerator is defined as the ratio of the energy absorbed at the evaporator to the energy required to perform the task.

$$(COP)_R = \frac{h_1 - h_4}{h_2 - h_1}$$

(b) Liquefaction of Gases

When a real gas which is initially at a temperature lower than the maximum inversion temperature is throttled, its temperature decreases. This principle is used by Linde in the Liquefaction of gases. Refer to figure 14.6 for understanding the operating cycle.

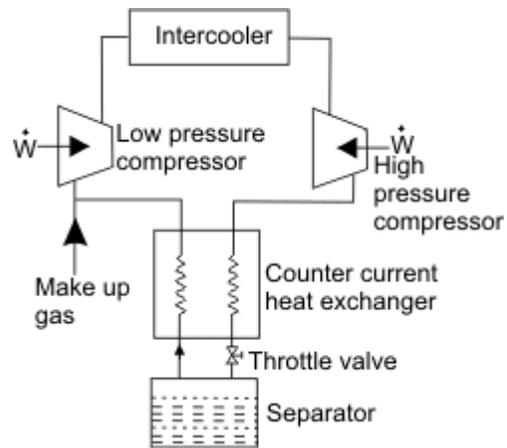


Figure 14.6

The gas is compressed to a high pressure and then cooled at constant pressure in a counter current heat exchanger with the cold gas which comes from the separator. The cooled gas is throttled to a low pressure. Thus some amount of gas is converted into the liquid phase. The two-phase mixture comes to the separator. The liquid is withdrawn and the cold gas is fed to the heat exchanger. Then the gas enters the compressor along with a fresh stream of make up gas for liquefaction.

Lecture 15 : Transient Flow Processes

The lecture contains

- Transient Flow Processes
- Charging of a Cylinder (Control Volume Analysis)
- Discharging of a cylinder (Control Volume Analysis)

Transient Flow Processes

During charging and discharging of cylinders/tanks the condition of the fluid inside the cylinders/tanks change with time. The rates of inflow and outflow of mass are not identical and there is accumulation of mass and energy inside the control volume.

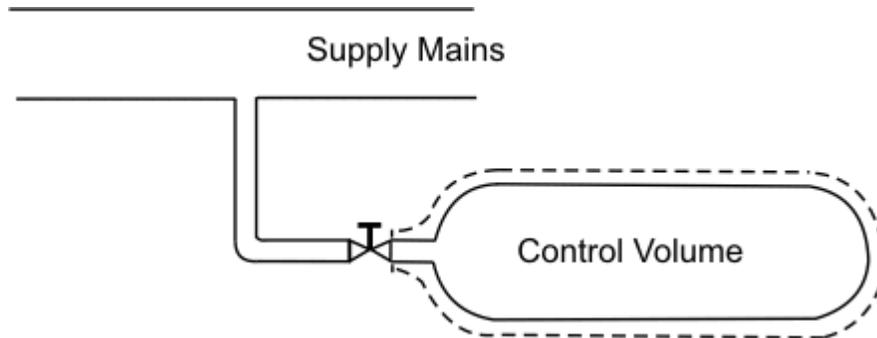


Figure 15.1

These processes are transient flow processes. The first law expression for a control volume is given by

$$\dot{m}_e \left(h_e + \frac{V_e^2}{2} + gZ_e \right) - \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gZ_i \right) = \dot{Q} - \dot{W}_{sh} - \frac{dE}{dt} \quad (15.1)$$

Charging of a Cylinder (control Volume Analysis)

While charging the cylinder from the supply mains, no gas leaves the control volume, and $\dot{m}_e = 0$. No shaft work is done; $\dot{W}_{sh} = 0$. Let us ignore the changes in the kinetic energy and potential energy of the gas during charging operation. Then it is possible to write from the equation (15.1)

$$-\dot{m}_i h_i = \dot{Q} - \frac{dE}{dt} \quad (15.2)$$

or,

$$-\dot{m}_i h_i = \dot{Q} - d(mu) / dt \quad (15.3)$$

Where, m denotes the mass of the gas in the control volume and u denotes the specific internal energy of the gas inside the control volume at time t . It is assumed that the state of the gas at any instant of time inside the control volume is uniform. The expression above can be integrated from the start of the charging operation ($t = 0$) to the end of the charging operation ($t = t$), to obtain

$$-h_i \int_0^t \dot{m}_i dt = \int_0^t \dot{Q} dt - \int_0^t [d(mu) / dt] dt \quad (15.4)$$

The principle of conservation of mass for the charging process reduces to:

$$\frac{dm}{dt} = \dot{m}_i \quad (15.5)$$

Rate of increase of mass in CV = Rate of mass entry

Integration of the above equation over time t gives the change of mass in the control volume during the charging operation

$$\int_0^t \dot{m}_i dt = \int_0^t \frac{dm}{dt} dt = (m_f - m_0) \quad (15.6)$$

Now in the equation (15.4), the last term on the RHS can be evaluated as

$$\int_0^t \left[\frac{d(mu)}{dt} \right] dt = m_f u_f - m_0 u_0 \quad (15.7)$$

and

$$\int_0^t \dot{Q} dt = Q \quad (15.8)$$

Substituting (15.6), (15.7), and (15.8) in (15.4) we get

$$(m_f - m_0) h_i = m_f u_f - m_0 u_0 - Q \quad (15.9)$$

If the cylinder is initially empty and the filling operation is carried out under adiabatic conditions the above expression reduces to

$$h_i = u_f \quad (15.10)$$

If the gas is treated as ideal ($h = c_p T$ and $u_f = c_v T_f$).

Then,

$$T_f = \gamma T_i \quad (15.11)$$

Where, T_f is the final temperature of the gas in the cylinder and γ is the ratio of the specific heats. T_i is the temperature of the gas in supply mains.

Discharging of a cylinder (control volume Analysis)

Consider a tank containing a gas at known conditions of temperature and pressure (figure 15.2).



Figure 15.2

The valve is opened, the gas escapes from the tank and the properties of the gas in the tank change with respect to time.

Let, P_0 = pressure of the gas inside the cylinder at $t = 0$

T_0 = temperature of the gas inside the cylinder at $t = 0$

u_0 = specific internal energy of the gas inside the cylinder at $t = 0$

P_f, T_f and u_f denote corresponding quantities of the gas left in the cylinder after the discharging operation.

V_e = velocity of the escaping gas. From the first law, we can write

$$\dot{m}_e \left[h_e + \frac{V_e^2}{2} + gz_e \right] - \dot{m}_i \left[h_i + \frac{V_i^2}{2} + gz_i \right] = \dot{Q} - \dot{W}_{sh} - \frac{dE}{dt} \quad (15.12)$$

No material flows into the cylinder $\dot{m}_i = 0$, $\dot{W}_{sh} = 0$ and the potential energy changes can be ignored. Then

$$\dot{m}_e \left[h_e + \frac{V_e^2}{2} \right] = \dot{Q} - \frac{dE}{dt} \quad (15.13)$$

For the discharging process, the conservation of mass gives

$$\frac{dm}{dt} = -\dot{m}_e \quad (15.14)$$

Integrating the above equation over time t gives

$$\int_0^t \frac{dm}{dt} dt = -\int_0^t \dot{m}_e dt = m_f - m_0 \quad (15.15)$$

Integration of the governing equation yields

$$\int_0^t \dot{m}_e \left(h_e + \frac{V_e^2}{2} \right) dt = \int_0^t \dot{Q} dt - \int_0^t \frac{dE}{dt} dt \quad (15.16)$$

Now the term on the left hand side may be evaluated as

$$\int_0^t \dot{m}_e \left(h_e + \frac{V_e^2}{2} \right) dt = (m_0 - m_f) \left(h_e + \frac{V_e^2}{2} \right) \quad (15.17)$$

Similarly,

$$\int_0^t \dot{Q} dt = Q \quad (15.18)$$

and

$$\int_0^t \frac{dE}{dt} dt = (m_f u_f - m_0 u_0) \quad (15.19)$$

Finally invoking (15.17), (15.18) and (15.19) in (15.16) we get

$$(m_0 - m_f) \left(h + \frac{V^2}{2} \right) = Q + m_0 u_0 - m_f u_f \quad (15.20)$$

It is assumed that the gas escapes with a uniform velocity V and specific enthalpy h .

Case of an Ideal Gas

Consider a small amount of gas in the cylinder (confined in an imaginary envelope) in the cylinder as a system.

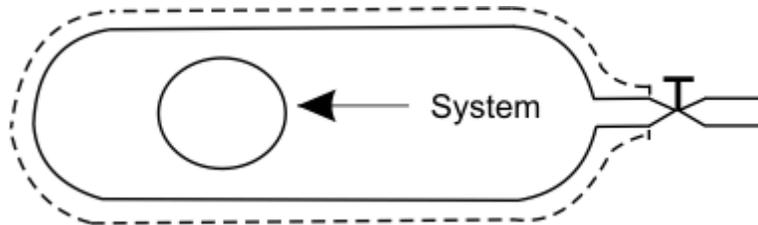


Figure 15.3

Imagine a situation when gas escapes the cylinder.

The boundary of the system changes continuously and eventually occupies the entire volume of the cylinder. The gas which is left in the cylinder does not exchange energy in the form of heat with the surroundings. It undergoes an adiabatic expansion. We can prove that the gas undergoes a reversible adiabatic expansion.

The general expression is:

$$\dot{m}_e \left[h_e + \frac{V_e^2}{2} + gz_e \right] - \dot{m}_i \left[h_i + \frac{V_i^2}{2} + gz_i \right] = \dot{Q} - \dot{W}_{sh} - \frac{dE}{dt} \quad (15.21)$$

We can change the basis of analysis from a control mass to a control volume based analysis. Under such a situation, Let us consider the cylinder volume as the volume of interest.

$\dot{Q} = 0$, $\dot{m}_i = 0$, $\dot{W}_{sh} = 0$, and ignore the change in KE and PE

$$\dot{m}_e h_e = - \frac{dE}{dt} = - \frac{d(mu)}{dt} \quad (15.22)$$

From the principle of conservation of mass

$$\dot{m}_e = - \frac{dm}{dt} \quad (15.23)$$

Therefore

$$- h_e \frac{dm}{dt} = - \frac{d(mu)}{dt} \quad (15.24)$$

For a perfect gas, $h = c_p T$ and $u = c_v T$. Then equation (15.24) can be rewritten as

$$c_p T \frac{dm}{dt} = c_v \frac{d(mT)}{dt} \quad (15.25)$$

or,

$$\gamma T \frac{dm}{dt} = m \frac{dT}{dt} + T \frac{dm}{dt} \quad (15.26)$$

or,

$$(\gamma - 1) T \frac{dm}{dt} = m \frac{dT}{dt} \quad (15.27)$$

or,

$$(\gamma - 1) \frac{dm}{m} = \frac{dT}{T} \quad (15.28)$$

By integration between final state and initial state

$$(\gamma - 1) \ln \left(\frac{m_f}{m_0} \right) = \ln \left(\frac{T_f}{T_0} \right) \quad (15.29)$$

As

$$PV = mRT \quad (15.30)$$

or,

$$m = \frac{PV}{RT} \quad (15.31)$$

Where R is the characteristics gas constant

So,

$$m_0 = \frac{P_0 V}{RT_0} \quad (15.32)$$

and

$$m_f = \frac{P_f V}{RT_f} \quad (15.33)$$

Invoking these relations, we get

$$\ln \left(\frac{P_f T_0}{P_0 T_f} \right) = \frac{1}{\gamma - 1} \ln \left(\frac{T_f}{T_0} \right) \quad (15.34)$$

or,

$$\ln \left(\frac{P_f}{P_0} \right) = \frac{\gamma}{\gamma - 1} \ln \left(\frac{T_f}{T_0} \right) \quad (15.35)$$

$$\frac{T_f}{T_0} = \left(\frac{P_f}{P_0} \right)^{\frac{\gamma - 1}{\gamma}} \quad (15.36)$$

Therefore the gas that remains in the tank can be considered to have undergone a reversible adiabatic expansion from the **initial pressure** P_0 to the **final pressure** P_f .

Lecture 16 :

The lecture contains

- Limitations of First Law of Thermodynamics
- Heat Engine
- Heat Pump
- Refrigerator
- KELVIN PLANCK STATEMENT

Limitations of First Law of Thermodynamics

The first law of thermodynamics is a law of conservation of energy. It does not specify the direction of the process. All spontaneous processes processed in one direction only. The first law of thermodynamics does not deny the feasibility of a process reversing itself. The first law of thermodynamics does not provide answers to the following questions.

IS A PARTICULAR PROCESS / REACTION FEASIBLE?

TO WHAT EXTENT DOES THE PROCESS / REACTION PROCEED?

IS COMPLETE CONVERSION OF INTERNAL ENERGY INTO WORK POSSIBLE?

There exists a law which determines the direction in which a spontaneous process proceeds. The law, known as the second law of thermodynamics, is a principle of wide generality and provides answer to the above questions.

It is essential to understand the meaning of the following terms in order to discuss the second law of thermodynamics:

- Thermal reservoir is a large body from which a finite quantity of energy can be extracted or to which a finite quantity of energy can be added as heat without changing its temperature.

- A source is a thermal reservoir at high temperature from which a heat engine receives the energy as heat.
- A sink is a low temperature thermal reservoir to which a heat engine rejects energy as heat.

Heat Engine

- A heat engine is a device which converts the energy it receives at heat, into work.
- It is a cyclically operating device.
- It receives energy as heat from a high temperature body, converts part of it into work and rejects the rest to a low temperature body.
- A thermal power plant is an example of a heat engine.

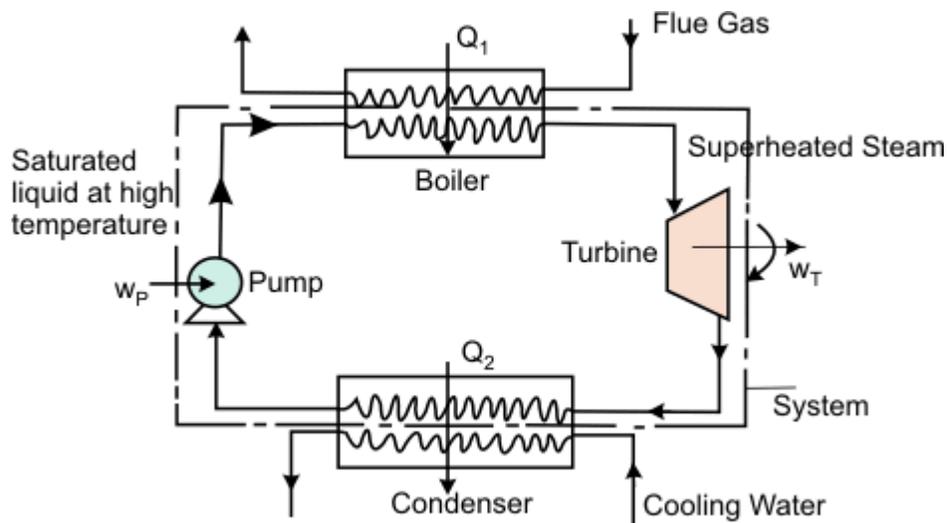


Figure 16.1

Figure 16.1 describes a basic arrangement of a thermal power plant

- In the boiler, the working fluid receives a certain amount of heat (Q_1) from the hot combustion products.
- The superheated steam enters a turbine where it undergoes expansion performing the shaft work W_T .

- The low pressure steam enters a condenser where it exchange energy as heat at constant pressure with the cooling water and emerges as the condensate. The condensate rejects a certain amount of heat (Q_2) to the cooling water.
- The low pressure condensate from the condenser enters the pump. Work (W_P) is done on the pump to elevate the condensate to the boiler pressure and return it to the boiler.

In the above example,

$$\text{Work done by the system} = W_T - W_P$$

$$\text{Energy absorbed as heat by the system} = Q_1$$

$$\text{Energy rejected as heat by the system} = Q_2$$

According to first law of thermodynamics, the heat and work interaction are related by the equation.

$$\oint dQ = \oint dW \quad (16.1)$$

Finally, the thermal efficiency (η) of a heat engine can be expressed as

$$\begin{aligned} \eta &= \frac{(\text{Energy absorbed as heat} - \text{Energy rejected as heat})}{\text{Energy absorbed as heat}} \\ &= \frac{\text{Net work done}}{\text{Energy absorbed as heat}} = \frac{W_T - W_P}{Q_1} \end{aligned}$$

or,

$$\eta = \frac{Q_1 - Q_2}{Q_1} \quad (16.2)$$

Heat Pump

Heat Pump is cyclically operating device which absorbs energy form a low temperature reservoir and reject energy as heat to a high temperature reservoir when work is performed on the device. Its objective is to reject energy as heat to a high temperature body (space heating in winter). The atmosphere acts as the low temperature reservoir.

Refrigerator

A refrigerator is a cyclically operating device which absorbs energy as heat from a low temperature body and rejects energy as heat to a high temperature body when work is performed on the device. The objective of this device is to refrigerate a body at low temperature. Usually it uses atmosphere as the high temperature reservoir.

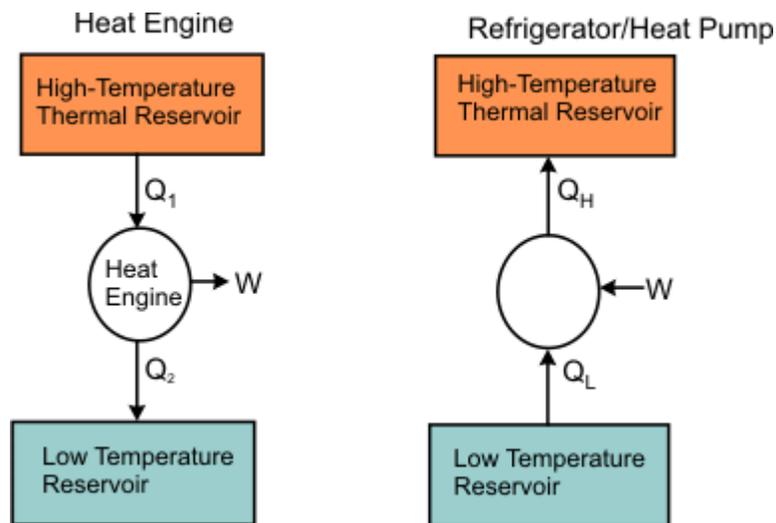


Figure 16.2

Refer to figure 16.2. Let Q_L and Q_H represents the amount of energy absorbed as heat from the low temperature reservoir and the energy rejected as heat to the high temperature reservoir respectively, Let W be the work done on the device to accomplish the task.

$$Q_H - Q_L = W \quad (16.3)$$

Therefore,

$$(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{(Q_H - Q_L)} \quad (16.4)$$

and

$$(COP)_{HP} = \frac{Q_H}{W} = \frac{Q_H}{(Q_H - Q_L)} \quad (16.5)$$

Heat engine and the refrigerator (/heat pump) can be represented as shown in Figure 16.2.

The efficiency of a heat engine is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = \frac{W_{net}}{Q_1} \quad (16.6)$$

$W_{net} < Q_1$ since Q_1 (heat) transferred to the system cannot be completely converted to work in a cycle. Therefore η is less than unity. A heat engine can never be 100 efficient. Therefore $Q_2 > 0$, i.e., there has always to be a heat rejection. Thus a heat engine has to exchange heat with two reservoirs, the source and the sink. This experience leads to the proposition of the second law of thermodynamics which has been stated in several different ways.

KELVIN PLANCK STATEMENT

It is impossible to construct a cyclically operating device such that it produces no other effect than the absorption of energy as heat from a single thermal reservoir and performs an equivalent amount of work.

The only option then is that the engine converts part of the energy it receives as heat into work and rejects the rest to another thermal reservoir the temperature of which is less than the temperature of the source. Two thermal reservoirs, one of high temperature (source), from which the working fluid receives energy as heat, and the other of low temperature (sink), to which the working fluid rejects energy as heat, are needed for a heat engine. Once the heat engine rejects a part of the energy it receives, its efficiency becomes less than one. Thus the Kelvin Planck statement further implies that no heat engine can have a thermal efficiency of one (hundred percent). This does not violate the first law of thermodynamics either.

Lecture 17 :

The lecture contains

- Kelvin - Planck Statement (Continued)
- Clausius Statement of the Second Law

Kelvin - Planck Statement (continued)

Second law restricts the thermal efficiency of a heat engine to less than one. It stipulates that some portion of the energy absorbed as heat from a source must always be rejected to a low temperature sink.

Wilhelm Ostwald introduced the concept of perpetual motion machine of the second kind (PMMSK or PMM2), that is, of a device which would perform work solely by absorbing energy as heat from a body. Such a device does not violate the first law of thermodynamics.

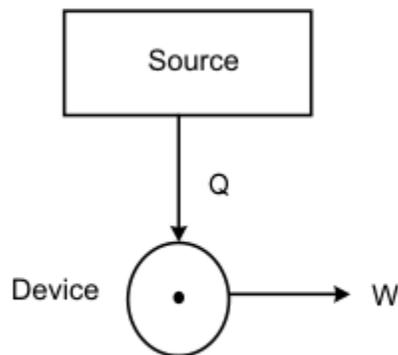


Figure 17.1

A PMMSK is a hypothetical device (Figure 17.1) which working cyclically, receives energy as heat from a single thermal reservoir, and delivers an equivalent amount of work. **The Kelvin-Planck statement of the second law** tells us that it is impossible to construct a perpetual motion machine of the second kind.

Clausius Statement of the Second Law

Heat always flows from a body at higher temperature to a body at a lower temperature. The reverse process never occurs spontaneously. Clausius' statement of the second law gives: *It is impossible to construct a device which, operating in a cycle, will produce no effect other than the transfer of heat from a low-temperature body to a high temperature body.*

This statement tells us that it is impossible for any device, unaided by an external agency, to transfer energy as heat from a cooler body to a hotter body. Consider the case of a refrigerator or a heat pump (Figure 17.2)

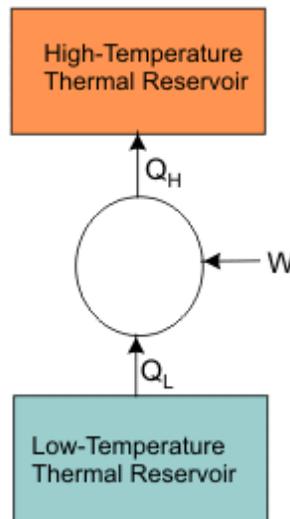


Figure 17.2

When $W = 0$,

$$(COP)_R \rightarrow \infty \text{ and}$$

$$(COP)_{HP} \rightarrow \infty$$

It is impossible to construct a refrigerator or a heat pump whose COP is infinity. Consider a domestic refrigerator, this device extracts energy as heat from the substance to be cooled and transfers it to the surroundings. The refrigerator is supplied with electric power. Energy transfer as heat from a high temperature body to a low temperature body is a spontaneous process. The Clausius statement of the second law of thermodynamics tells that this spontaneous process cannot proceed in the reverse direction.

Apparently, the Kelvin Planck statement and the Clausius statement of the second law of thermodynamics are altogether different. They are not ! Instead, they are equivalent. A violation of Kelvin Planck statement leads to a violation of the Clausius statement too and vice-versa.

Clausius Statement of the Second Law (contd...)

Let us suppose that the Kelvin Planck statement is incorrect.

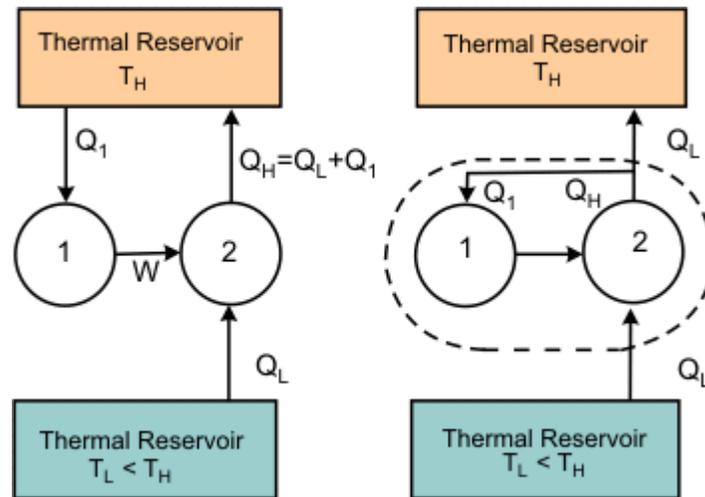


Figure 17.3

Refer to Figure 17.3 that is, it is possible to construct a device I which, working cyclically, absorbs energy a heat (Q_1) from a source at temperature T_H and performs an equivalent amount of work ($W = Q_1$). Next consider a device II which absorbs Q_L amount of energy from a low temperature body at T_L and delivers energy as heat Q_H to a high temperature reservoir at T_H . To accomplish this, work W is done on the device. The device II does not violate the Clausius statement. For device II, we can write $Q_H = Q_L + W$. Now combine I and II. The work delivered by device I is used by device, II.

Then

$$W = Q_1, \tag{17.1}$$

$$Q_H = Q_L + W = Q_L + Q_1 \tag{17.2}$$

This combined device (which is no more aided by any external agency) working cyclically, is not producing any effect other than the transfer of energy as heat (Q_L) from the low temperature reservoir to the high temperature reservoir. This is in violation of the Clausius statement.

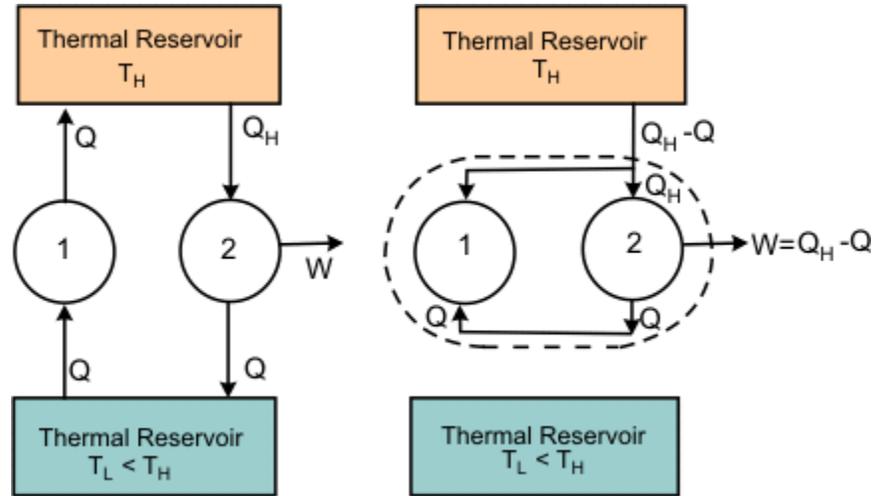


Figure 17.4

To prove that violation of the Clausius' statement leads to violation of Kelvin Planck statement, let us assume that the Clausius' statement is incorrect. That is, it is possible to construct a device I (refer to Figure 17.4) such that it transfers energy as heat (Q) from a body at lower temperature to a body at higher temperature unaided by any external agency. Consider another device II which receives energy as heat (Q_H) from a body at higher temperature, delivers work (W) and rejects energy as heat (Q) to the body at a low temperature. Device II does not violate Kelvin Planck statement. Application of the first law of thermodynamics to device II gives,

$$Q_H = Q_L + W \quad (17.3)$$

Now consider the combination of devices I and II as a single device. This combined device, working cyclically, absorbs ($Q_H - Q$) amount of energy as heat from the thermal reservoir at temperature T_H and delivers work ($W = Q_H - Q$), leaving the thermal reservoir at temperature T_L unaffected. That is, the resulting device is a PMMSK, which is in violation of the Kelvin Planck statement. Thus the Kelvin Planck statement and the Clausius' statement are equivalent.

Lecture 18 : Reversibility, Irreversibility and Carnot cycle

The lecture contains

- Introduction
- Irreversible Processes
- Reversible Processes
- Carnot Cycle
- Carnot Engine

Reversibility, Irreversibility and Carnot cycle

The second law of thermodynamics distinguishes between reversible and irreversible processes.

- If a process can proceed in either direction without violating the second law of thermodynamics, it is reversible process. A reversible process is carried out infinitely slowly with an infinitesimal gradient, so that every state passed through by the system is an equilibrium state. So, a reversible process is a quasi-static process which can proceed in either direction.
- Given a process, if the attempt to reverse its direction leads to a violation of the second law of thermodynamics, then the given process is irreversible.

Any natural process carried out with a finite gradient is an **irreversible process**. A reversible process which consists of a succession of equilibrium states, is an idealized hypothetical process, approached only as a limit. **It is said to be an asymptote to reality**, All spontaneous processes are irreversible.

Irreversible Processes

The examples of irreversible processes are: Motion with friction, free expansion, Expansion/ compression with finite pressure difference, Energy transfer as heat with finite ΔT , Mixing of matter at different states, Mixing of non-identical gases.

Reversible Processes

The processes which can be idealized as reversible are: Motion without friction, Expansion/compression with infinitesimal pressure difference, Energy transfer as heat with infinitesimal temperature difference.

Carnot Cycle

A French engineer Sadi Carnot was the first to introduce the idea of reversible cycle. From the second law, it has been observed that the efficiency of a heat engine is less than unity. If the efficiency of heat engine is less than unity, what is the maximum efficiency of a heat engine? This can be answered by considering the Carnot cycle. The concept of carnot cycle is executed via Carnot engine.

Carnot Engine

Let us consider the operation of a hypothetical engine which employs the Carnot cycle. The Carnot engine consists of a **cylinder-piston assembly** in which a certain amount of gas(working fluid) is enclosed. Refer to Figure 18.1 representing the Carnot cycle.

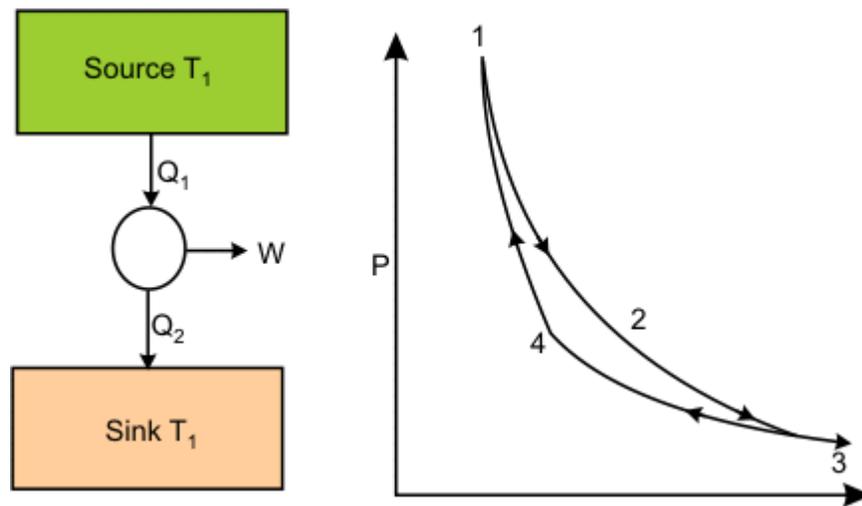


Figure 18.1

Reversible Isothermal Heat Addition

In the first process, the cylinder head is brought into contact with a source at temperature T_1 . The gas inside the cylinder is also at temperature T_1 . The gas expands **reversibly and isothermally**. During this process, the system absorbs energy as heat (Q_1) from the source. The system changes its state from 1 to 2 on the $P-v$ diagram.

$$Q_1 = (U_2 - U_1) + W_{1-2} \quad (18.1)$$

where, for an ideal gas, $U_2 = U_1$

Reversible Adiabatic Expansion

In the second process, the cylinder head is insulated and the gas is allowed to expand till its temperature is equal to the sink temperature T_2 . The system thus reaches state 3. **This is a reversible adiabatic process.**

$$0 = (U_3 - U_2) + W_{2-3} \quad (18.2)$$

Reversible Isothermal Heat Rejection

In the next process, the system is brought into contact with the sink which is at a temperature T_2 . The heat Q_2 leaves the system and the internal energy further decreases

$$-Q_2 = (U_4 - U_3) - W_{3-4} \quad (18.3)$$

where, only for an ideal gas, $U_4 = U_3$

Through a reversible isothermal process the system reaches state 4.

Reversible Adiabatic Compression

In the next process, the gas is compressed reversibly and adiabatically till it reaches the initial state 1, thus, completing the cycle.

$$0 = U_1 - U_4 - W_{4-1} \quad (18.4)$$

Summing up all the processes, one can write

$$Q_1 - Q_2 = (W_{1-2} + W_{2-3}) - (W_{3-4} + W_{4-1})$$

or,

$$\sum_{cycle} Q_{net} = \sum_{cycle} W_{net}$$

The thermal efficiency,

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (18.5)$$

Efficiency of Carnot Engine Using Ideal Gas

1-2: A reversible isothermal expansion with heat addition

$$Q_1 = \int_1^2 P dv = RT_1 \ln\left(\frac{v_2}{v_1}\right) \quad (18.6)$$

2-3: A reversible adiabatic expansion

$$W = c_v(T_1 - T_2) \quad (18.7)$$

3-4: A reversible isothermal compression with heat rejection

$$Q_2 = \int_3^4 P dv = RT_2 \ln\left(\frac{v_4}{v_3}\right) \quad (18.8)$$

4-1: A reversible adiabatic compression

$$W = \int_4^1 du = c_v(T_2 - T_1) \quad (18.9)$$

$$\begin{aligned} \Sigma W &= RT_1 \ln\left(\frac{\hat{v}_2}{\hat{v}_1}\right) + c_v(T_1 - T_2) + RT_2 \ln\left(\frac{v_4}{v_3}\right) + c_v(T_2 - T_1) \\ &= RT_1 \ln\left(\frac{v_2}{v_1}\right) + RT_2 \ln\left(\frac{v_4}{v_3}\right) \end{aligned} \quad (18.10)$$

Energy absorbed as heat

$$Q_1 = RT_1 \ln(v_2/v_1) \quad (18.11)$$

Thermal efficiency,

$$\eta = 1 + \frac{RT_2 \ln(v_4/v_3)}{RT_1 \ln(v_2/v_1)} \quad (18.12)$$

Here, for the ideal gases we can write

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_3} \right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_4} \right)^{\gamma-1}$$

Also,

$$\frac{v_2}{v_3} = \frac{v_1}{v_4}$$

or,

$$\frac{v_2}{v_1} = \frac{v_3}{v_4} \tag{18.13}$$

So,

$$\eta = 1 - \frac{T_2}{T_1} \frac{\ln(v_2 / v_1)}{\ln(v_2 / v_1)} = 1 - \frac{T_2}{T_1} \tag{18.14}$$

Lecture 19 : Carnot's Principles (Theorems)

The lecture contains

- Carnot's Principle I
- Carnot's Principle II

Two consequences of the second law of thermodynamics are will known as Carnot's principles.

Principle I:

No heat engine operating between the two given thermal reservoirs, each of which is maintained at a constant temperature, can be more efficient than a reversible engine operating between the same two thermal reservoirs. Refer to Figure 19.1

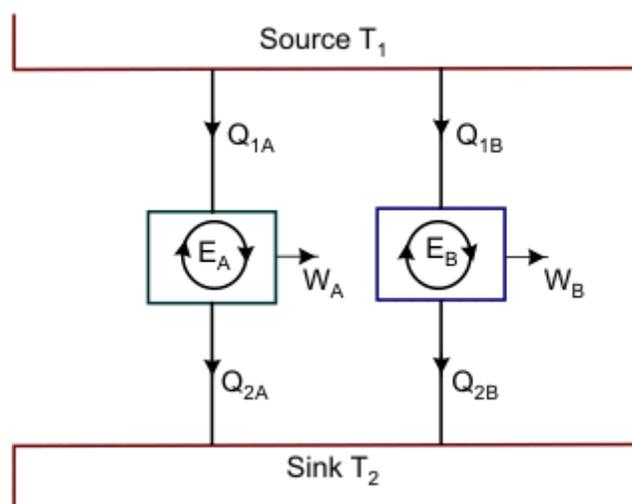


Figure 19.1

Let two heat engines E_A and E_B operate between the given source at temperature T_1 and the given sink at temperature T_2 as shown.

Let E_A be any heat engine and E_B any reversible heat engine. We are to prove that the efficiency of E_B is more than that of E_A . Let us assume that it is not true $\eta_A > \eta_B$. Let the rates of working of the engines be such that

$$Q_{1A} = Q_{1B} = Q_1 \quad (19.1)$$

Since,

$$\eta_A > \eta_B \Rightarrow \frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}; \text{ or, } W_A > W_B \quad (19.2)$$

Now let the direction of E_B be reversed.

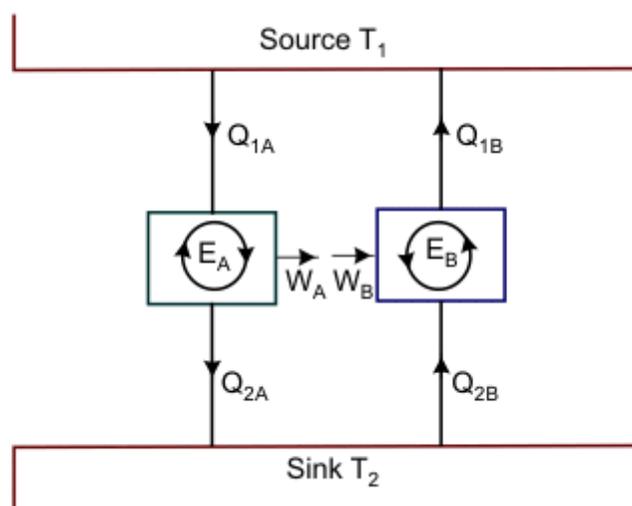


Figure 19.2

Refer to Figure 19.2. Since E_B is a reversible heat engine, the magnitudes of heat and work quantities will remain the same, but their directions will be reversed as shown.

Since $W_A > W_B$ some part of W_A (equal to W_B) may be fed to drive the reversed heat engine E_B . Since, $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by the reversed E_B may be supplied to E_A .

The source may, therefore, be eliminated. The net result is that E_A and E_B together constitute a heat engine which, operating in a cycle, produces net work $W_A - W_B$, while exchanging heat with a single reservoir at T_2 .

This violates the Kelvin-Planck statement of the second law . Hence the assumption $\eta_A > \eta_B$ is wrong.

Therefore,

$$\eta_B \geq \eta_A \tag{19.3}$$

Principle II:

All reversible heat engines operating between the two given thermal reservoirs have the same efficiency. The efficiency of reversible heat engine does not depend on the working fluid, it depends only on the temperature of the reservoirs between which it operates.

To prove the proposition, let us assume that the efficiency of the reversible engine R_1 is greater than the efficiency of the reversible engine R_2 .

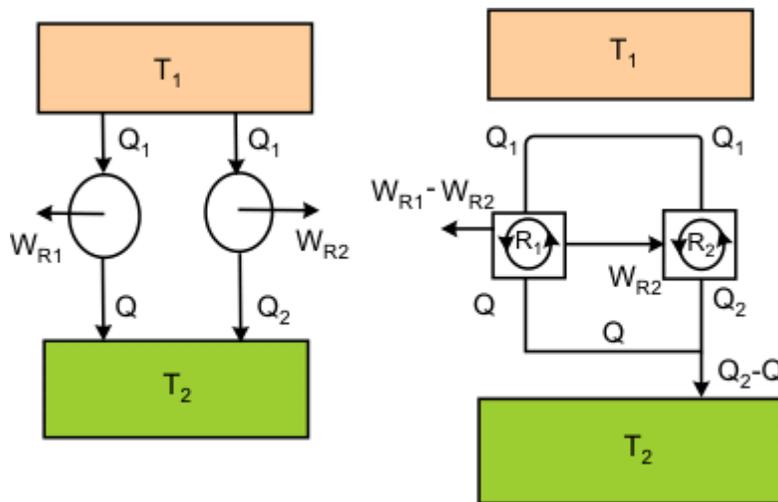


Figure 19.3

Refer to Figure 19.3. The engine R_1 absorbs energy as heat Q_1 from the constant temperature thermal reservoir at T_1 , does work W_{R1} and rejects energy as heat Q to the reservoir at T_2 . The engine R_2 absorbs energy as heat Q_1 from the reservoir at T_1 , does

work W_{R2} and rejects energy as heat Q_2 to the reservoir at T_2 . Then $W_{R1} = Q_1 - Q$, and $W_{R2} = Q_1 - Q_2$

$$\eta_{R1} = W_{R1} / Q_1 = 1 - \frac{Q}{Q_1} \quad (19.4)$$

and

$$\eta_{R2} = W_{R2} / Q_1 = 1 - \frac{Q_2}{Q_1} \quad (19.5)$$

By assumption, $\eta_{R1} > \eta_{R2}$

Then,

$$\left(1 - \frac{Q}{Q_1}\right) > \left(1 - \frac{Q_2}{Q_1}\right) \text{ or } Q < Q_2 \quad (19.6)$$

Therefore, $W_{R1} > W_{R2}$

Since R_2 is a reversible engine, it can be made to execute the cycle in the reversed order. That is, when work W_{R2} is performed on the device, it absorbs energy as heat, Q_2 from the reservoir at T_2 and rejects energy as heat Q_1 to the reservoir at T_1 . Since, $W_{R1} > W_{R2}$, R_2 can be run as a heat pump utilizing **part of the work done by R_1** . The combination of the two devices is also shown in the figure.

The net work done by the device is given by

$$W_{R1} - W_{R2} = (Q_1 - Q) - (Q_1 - Q_2) = Q_2 - Q \quad (19.7)$$

- The resulting device absorbs energy as heat $(Q_2 - Q)$ from the reservoir at T_2 .
- Does not require any interaction with the second reservoir.
- Delivers an equivalent amount of work.

This is in violation of the Kelvin-Planck statement of the second law of thermodynamics.

Hence the assumption that $\eta_{R1} > \eta_{R2}$, is incorrect. Therefore,

$$\eta_{R2} \geq \eta_{R1} \quad (19.8)$$

Now let us assume that the reversible engine R_2 is more efficient than the reversible engine R_1 . Then the reversible engine R_1 can be run as a heat pump, utilizing the part of the work done by R_2 . By following the similar argument as the earlier case, we can arrive at the result that,

$$\eta_{R1} \geq \eta_{R2} \quad (19.9)$$

Hence, it can be concluded that

$$\eta_{R1} = \eta_{R2} \quad (19.10)$$

Stated in words: All reversible engines operating between the two given thermal reservoirs have the same efficiency.

Lecture 20 : Thermodynamic Temperature Scale

The lecture contains

- Thermodynamic Temperature Scale

Thermodynamic Temperature Scale

A temperature scale, which does not depend on the thermodynamic property of the substance can be established by making use of the fact that the efficiency of a reversible heat engine does not depend on the nature of the working fluid but depends only upon the temperature of the reservoirs between which it operates. The establishment of thermodynamic temperature scale is also a consequence of the second law of thermodynamics. Refer to Figure 20.1.

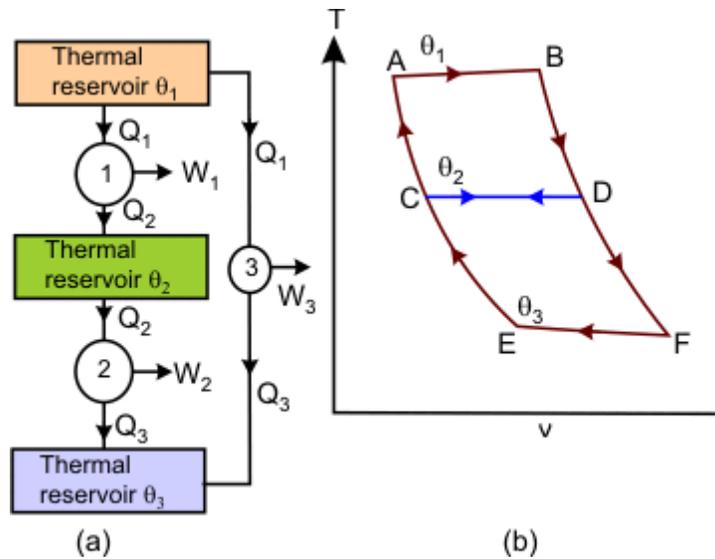


Figure 20.1

Let, θ_1, θ_2 and θ_3 be the isotherms. Let the two reversible adiabats intersect the three isotherms. Let the reversible engine 1 absorb energy as heat, Q_1 from the reservoir at θ_1 and reject energy as heat, Q_2 to the reservoir at θ_2 . Let the reversible engine 2 absorb energy as heat, Q_2 from the reservoir θ_2 and reject heat, Q_3 to the reservoir at θ_3 . Let W_1 and W_2 represent the work done by engines 1 and 2, respectively. Let a third Carnot engine absorb energy as heat Q_1 from the reservoir at θ_1 and reject energy as heat Q_3 to the reservoir at θ_3 . The work done by the engine is given by

$$W_3 = W_1 + W_2 \quad (20.1)$$

Also,

$$\eta_1 = 1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2) \quad (20.2)$$

or,

$$\frac{Q_2}{Q_1} = 1 - f(\theta_1, \theta_2) \quad (20.3)$$

or,

$$F(\theta_1, \theta_2) = \frac{Q_1}{Q_2} \quad (20.4)$$

Now,

$$\eta_2 = 1 - \frac{Q_3}{Q_2} = f(\theta_2, \theta_3) \quad (20.5)$$

or,

$$\frac{Q_3}{Q_2} = 1 - f(\theta_2, \theta_3) \quad (20.6)$$

or,

$$F(\theta_2, \theta_3) = \frac{Q_2}{Q_3} \quad (20.7)$$

Similarly,

$$\eta_3 = 1 - \frac{Q_3}{Q_1} = f(\theta_1, \theta_3) \quad (20.8)$$

or,

$$\frac{Q_3}{Q_1} = 1 - f(\theta_1, \theta_3) \quad (20.9)$$

or,

$$F(\theta_1, \theta_3) = \frac{Q_1}{Q_3} \quad (20.10)$$

Then,

$$\frac{Q_1}{Q_2} = \frac{(Q_1/Q_3)}{(Q_2/Q_3)} \quad (20.11)$$

or,

$$F(\theta_1, \theta_2) = \frac{F(\theta_1, \theta_3)}{F(\theta_2, \theta_3)} \quad (20.12)$$

In the above equation, θ_3 does not appear on the left hand side. Therefore, on the right hand side, the dependence on θ_3 should cancel out. Hence, the nature of function F is such that,

$$F(\theta_1, \theta_2) = \phi(\theta_1)\psi(\theta_2) \quad (20.13)$$

Then,

$$\phi(\theta_1)\psi(\theta_2) = \frac{\phi(\theta_1)\psi(\theta_3)}{\phi(\theta_2)\psi(\theta_3)} = \frac{\phi(\theta_1)}{\phi(\theta_2)} \quad (20.14)$$

Therefore,

$$\psi(\theta_2) = 1/\phi(\theta_2)$$

or,

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \quad (20.15)$$

So,

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2) = \phi(\theta_1) / \phi(\theta_2) \quad (20.16)$$

There is no further restriction on the function. The choice of the function ϕ now defines the temperature scale of interest.

If we choose

$$\phi(\theta) = \theta \quad (20.17)$$

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} \quad (20.18)$$

or,

$$\frac{\text{Energy absorbed by a Carnot engine}}{\text{Energy rejected by a Carnot engine}} = \frac{\theta_1}{\theta_2} \quad (20.19)$$

Recall,

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (20.20)$$

or,

$$\eta = 1 - \frac{\theta_2}{\theta_1} \quad (20.21)$$

The efficiency of no heat engine can be greater than one. The lowest possible temperature in this scale is zero ($\theta_2 = 0$).

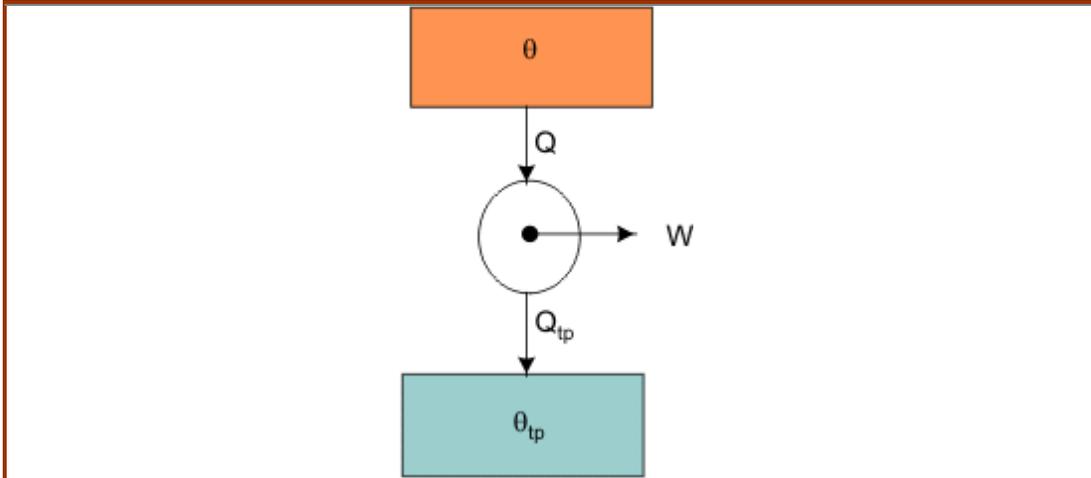


Figure 20.2

Refer to Figure 20.2. Hence it is called the absolute temperature scale. The absolute temperature scale is also known as Kelvin temperature scale. In defining the Kelvin temperature scale also, the triple point of water is taken as the standard reference point. For a Carnot engine operating between reservoirs at temperature θ and θ_{tp} , θ_{tp} being the triple point of water arbitrarily assigned the value of 273.16 K ,

$$\frac{Q}{Q_{tp}} = \frac{\theta}{\theta_{tp}}$$

or,

$$\theta = 273.16 \frac{Q}{Q_{tp}} \quad (20.22)$$

If this equation is compared with the perfect gas temperature scale

[remember, we have obtained $T = 273.16 \lim_{P_{tp} \rightarrow 0} \left(\frac{P}{P_{tp}} \right)$, it is seen that in the Kelvin Scale Q plays the role of the thermometric property.

Consider a Carnot engine using a perfect gas as a working fluid. Let the high temperature reservoir be at T_1 and low temperature reservoir be at T_2

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad (20.23)$$

or,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

But the absolute temperature scale is defined by the relation

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} \quad (20.24)$$

Therefore,

$$\frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}$$

Since the numerical value $(273.16K)$ assigned to the triple point of water can be chosen to be same for both the perfect gas scale and the absolute temperature scale, $\theta = T$. Hereafter, the common symbol T may be used to represent the temperature.

