Subject Title	BASIC THERMODYNAMICS		
Subject Code	17ME33	**CIA Marks**	40
No of Lecture Hrs + Practical Hrs / Week	4	**SEE Marks**	60
Total No of Lecture + Practical Hrs	50	**Exam Hours**	03
			CREDITS – 04

COURSE OBJECTIVES

1. Learn about thermodynamic systems and boundaries
2. Study the basic laws of thermodynamics including, conservation of mass, conservation of energy or first law , second law and Zeroth law.
3. Understand various forms of energy including heat transfer and work
4. Identify various types of properties (e.g., extensive and intensive properties)
5. Use tables, equations, and charts, in evaluation of thermodynamic properties
6. Apply conservation of mass, first law, and second law in thermodynamic analysis of systems (e.g., turbines, pumps, compressors, heat exchangers, etc.)
7. Enhance their problem solving skills in thermal engineering

Module -1

Fundamental Concepts & Definitions

Thermodynamics definition and scope, Microscopicand Macroscopic approaches. Some practical applications of engineering thermodynamic Systems, Characteristics of system boundary and control surface, examples. Thermodynamic properties; definition and units, intensive and extensive properties. Thermodynamic state, state point, state diagram, path and process, quasi-static process, cyclic and non-cyclic ;processes; Thermodynamic equilibrium; definition, mechanical equilibrium; diathermic wall, thermal equilibrium, chemical equilibrium, Zeroth law of thermodynamics, Temperature; concepts, scales, fixed points and measurements.

Work and Heat

Mechanics, definition of work and its limitations.Thermodynamicdefinition of work; examples, sign convention. Displacement work; as a part of a system boundary, as a whole of a system boundary, expressions for displacement work in various processes through p-v diagrams. Shaft work; Electrical work.Other types of work.Heat; definition, units and sign convention.

10 Hours

Module -2

First Law of Thermodynamics

Joules experiments, equivalence of heat and work.Statement of the First law of thermodynamics, extension of the First law to non - cyclic processes, energy, energy as a property, modes of energy, pure substance; definition, two-property rule, Specific heat at constant volume, enthalpy, specific heat at constant pressure. Extension of the First law to control volume; steady state-steady flow energy equation, important applications, analysis of unsteady processes such as film and evacuation of vessels with and without heat transfer.

Second Law of Thermodynamics

Devices converting heat to work; (a) in a thermodynamiccycle, (b) in a mechanical cycle. Thermal reservoir. Direct heat engine; schematic representation and efficiency. Devices converting work to heat in a thermodynamic cycle; reversed heat engine, schematic representation, coefficients of performance. Kelvin - Planck statement of the Second law of Thermodynamics; PMM I and PMM II, Clausius statement of Second law of Thermodynamics, Equivalence of the two statements; Reversible and irreversible processes; factors that make a process irreversible, reversible heat engines, Carnot cycle, Carnot principles.

10 Hours

Module -3

Entropy

Clasius inequality; Statement, proof, application to a reversible cycle. Entropy; definition, a property, change of entropy, principle of increase in entropy, entropy as a quantitative test for irreversibility, calculation of entropy using Tds relations, entropy as a coordinate. Available and unavailable energy.

Pure Substances

P-T and P-V diagrams, triple point and critical points.Subcooled liquid,saturated liquid, mixture of saturated liquid and vapour, saturated vapour and superheated vapour states of pure substance with water as example. Enthalpy of change of phase (Latent heat).Dryness fraction (quality), T-S and H-S diagrams, representation of various processes on these diagrams.Steam tables and its use.Throttling calorimeter, separating and throttling calorimeter.

10 Hours

Module -4

Thermodynamic relations

Helmholtz and Gibbs functions, Maxwell relation, ClausiusClayperon's equation. Ideal gas;equation of state, internal energy and enthalpy as functions of temperature only, universal and particular gas constants, specific heats, perfect and semi-perfect gases. Evaluation of heat, work, change in internal energy.enthalpy and entropy in various quasi-static processes.

10Hours

Module -5

Ideal gas mixture

Ideal gas mixture; Dalton's laws of partial pressures, Amagat's law ofadditive volumes, evaluation of properties, Analysis of various processes. Real Gases: Introduction. Vander Waal's Equation of state, Van-der Waal's constants in terms of critical properties, Law of corresponding states, compressiblity factor; compressibility chart, RedllichKwong equation, Beattie-bridgeman equation.

10 Hours

Data Handbooks :

1. Thermodynamic data hand book, B.T. Nijaguna.
2. Properties of Refrigerant & Psychometric(tables & Charts in SI Units), Dr.S.S. Banwait, Dr. S.C. Laroiya, Birla Pub. Pvt. Ltd., Delhi, 2008

TEXT BOOKS:

1. Thermodynamics, An Engineering Approach, YunusA.Cenegal and Michael A.Boles,Tata McGraw Hill publications, 2002
2. Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.

REFERENCE BOOKS:

1. Engineering Thermodynamics, J.B.Jones and G.A.Hawkins, John Wiley and Sons..
2. Fundamentals of Classical Thermodynamics, G.J.VanWylen and R.E.Sonntag, Wiley Eastern.
3. An Introduction to Thermodynamics, Y.V.C.Rao, Wiley Eastern, 1993,
4. B.K Venkanna, Swati B. Wadavadagi “Basic Thermodynamics, PHI,New Delhi, 2010

COURSE OUTCOMES:

1. Students will be able to acquire the fundamentals of thermodynamics, its laws, energy interactions, various temperature scales and its measurements
2. Students will be able to analyze and apply the laws of thermodynamics to various physical problems
3. Students will be able to interpret the behavior of pure substance and its applications to practical problems
4. Students will be equipped with the various thermodynamic relations and its applications to ideal gas mixtures

MODULE -1
FUNDAMENTAL CONCEPTS & DEFINITIONS

Thermodynamics involves the storage, transformation, and transfer of energy. Energy is stored as internal energy (due to temperature), kinetic energy (due to motion), potential energy (due to elevation), and chemical energy (due to chemical composition); it is transformed from one of these forms to another; and it is transferred across a boundary as either heat or work. We will present equations that relate the transformations and transfers of energy to properties such as temperature, pressure, and density. The properties of materials thus become very important. Many equations will be based on experimental observations that have been presented as mathematical statements, or laws: primarily the first and second laws of thermodynamics.

The mechanical engineers objective in studying thermodynamics is most often the analysis of a rather complicated device, such as an air conditioner, an engine, or a power plant. As the fluid flows through such a device, it is assumed to be a continuum in which there are measurable quantities such as pressure, temperature, and velocity. This book, then, will be restricted to macroscopic or engineering thermodynamics. If the behavior of individual molecules is important, statistical thermodynamics must be consulted.

Macroscopic Vs Microscopic Viewpoint

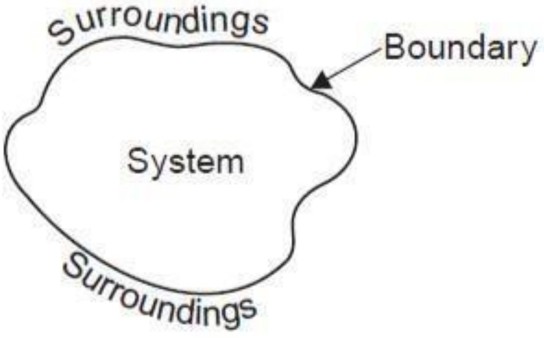
There are two points of view from which the behavior of matter can be studied: the macroscopic and the microscopic. In the macroscopic approach, a certain quantity of matter is considered, without the events occurring at the molecular level being taken into account. From the microscopic point of view, matter is composed of myriads of molecules. If it is a gas, each molecule at a given instant has a certain position, Velocity and energy, and for each molecule these change very frequently as a result of collisions. The behavior of the gas is described by summing up the behavior of each molecule. Such a study is made in microscopic or statistical thermodynamics. Macroscopic thermodynamics is only concerned with the effects of the action of many molecules, and these effects can be perceived by human senses. For example, the macroscopic quantity, Pressure, is the average rate of change of momentum due to all the molecular collisions made on a unit area. The effects of pressure can be felt. The macroscopic point of view is not concerned with the action of individual molecules, and the force on a given unit area can be measured by using, e.g., Pressure gauge.

System:

We need to fix our focus of attention in order to understand heat and work interaction. The body or assemblage or the space on which our attention is focused is called system. The system may be having real or imaginary boundaries across which the interaction occurs. The boundary may be rigid and sometimes take different shapes at different times. If the system has imaginary boundary then we must properly formulate the idea of system in our mind.

Surroundings:

Everything else apart from system constitutes surroundings. The idea of surroundings gets formulated the moment we define system. System and surroundings together form what is known as universe.



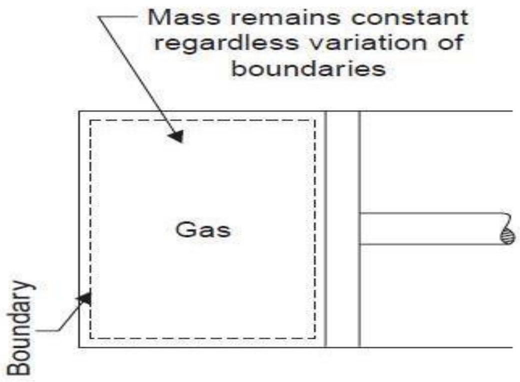
The system.

Closed system:

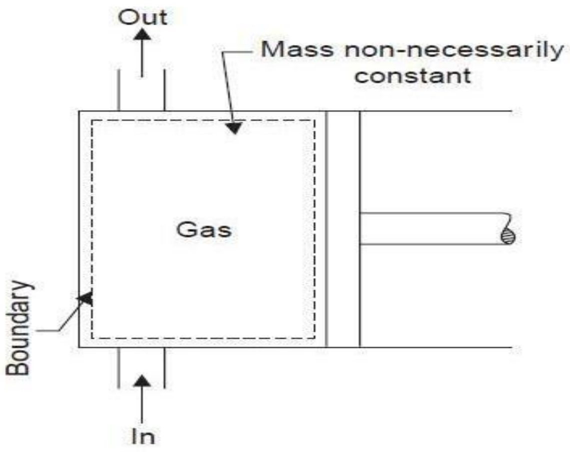
If the system has a boundary through which mass or material cannot be transferred, but only energy can be transferred is called closed system. In an actual system, there may not be energy transfer. What is essential for the system to be closed is the inability of the boundary to transfer mass only.

Open system:

If the system has a boundary through which both energy and mass can transfer, then it is called open system.



Closed system.



Open system.

Isolated System

An isolated system is that system which exchanges neither energy nor matter with any other system or with environment.

Properties:

Variables such as pressure, temperature, volume and mass are properties. A system will have a single set of all these values.

Intensive properties:

The properties that are independent of amount contained in the system are called extensive properties. For example, take temperature. We can have a substance with varying amount but still same temperature. Density is another example of intensive property because density of water is same no matter how much is the water. Other intensive properties are pressure, viscosity, surface tension.

Extensive properties:

The properties that depend upon amount contained in the system are called extensive properties. Mass depends upon how much substance a system has in it therefore mass is an extensive property.

State:

It is defined as condition of a system in which there are one set of values for all its properties. The properties that define the state of a system are called state variables.

There is certain minimum number of intensive properties that requires to be specified in order to define the state of a system and this number is uniquely related to the kind of system. This relation is phase rule which we shall discuss little later.

Process:

The changes that occur in the system in moving the system from one state to the other is called a process. During a process the values of some or all state variables change. The process may be accompanied by heat or work interaction with the system.

Equilibrium state:

A system is said to be in thermodynamic equilibrium if it satisfies the condition for thermal equilibrium, mechanical equilibrium and also chemical equilibrium. If it is in equilibrium, there are no changes occurring or there is no process taking place.

Thermal equilibrium:

There should not be any temperature difference between different regions or locations within the system. If there are, then there is no way a process of heat transfer does not take place. Uniformity of temperature throughout the system is the requirement for a system to be in thermal equilibrium.Surroundings and the system may be at different temperatures and still system may be in thermal equilibrium.

Mechanical equilibrium:

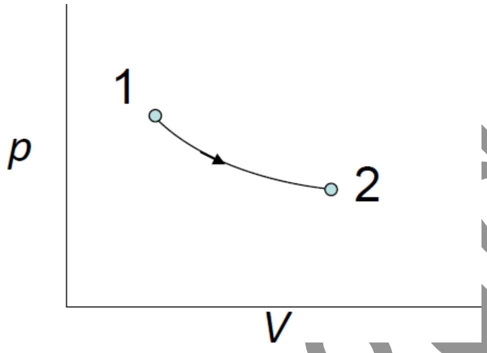
There should not be any pressure difference between different regions or locations within the system. If there are, then there is no way a process of work transfer does not take place. Uniformity of pressure throughout the system is the requirement for a system to be in mechanical equilibrium.Surroundings and the system may be at pressures and still system may be in mechanical equilibrium.

Chemical equilibrium:

There should not be any chemical reaction taking place anywhere in the system, then it is said to be in chemical equilibrium. Uniformity of chemical potential throughout the system is the requirement for a system to be in chemical equilibrium.Surroundings and the system may have different chemical potential and still system may be in chemical equilibrium.

Thermodynamic process:

A system in thermodynamic equilibrium is disturbed by imposing some driving force; it undergoes changes to attain a state of new equilibrium. Whatever is happening to the system between these two equilibrium state is called a process. It may be represented by a path which is the locus all the states in between on a p-V diagram as shown in the figure below.



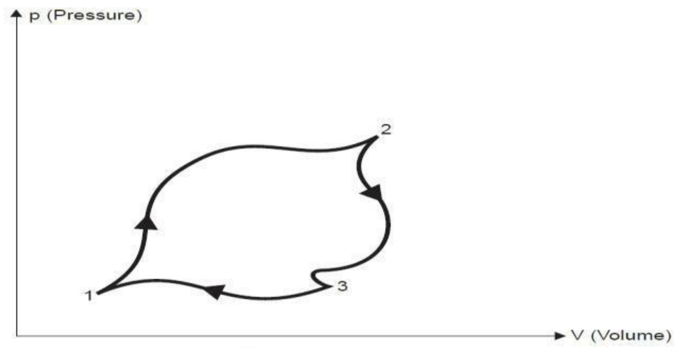
For a system of gas in piston and cylinder arrangement which is in equilibrium, altering pressure on the piston may be driving force which triggers a process shown above in which the volume decreases and pressure increases. This happens until the increasing pressure of the gas equalizes that of the surroundings. If we locate the values of all intermediate states, we get the path on a p-V diagram.

Quasi-static process:

Quasi means „almost‟ . A quasi-static process is also called a reversible process. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.

CYCLE

Any process or series of processes whose end states are identical is termed a cycle.



Cycle of operations.

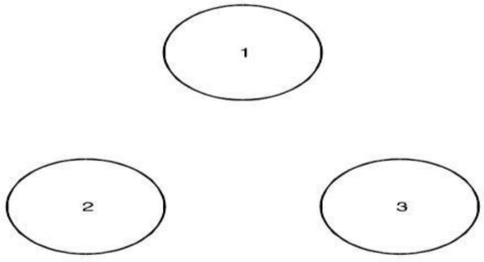
TEMPERATURE

The temperature is a thermal state of a body which distinguishes a hot body from a cold body. The temperature of a body is proportional to the stored molecular energy i.e., the average molecular kinetic energy of the molecules in a system. (A particular molecule does not have a temperature, it has energy. The gas as a system has temperature). Instruments for measuring ordinary temperatures are known as **thermometers** and those for measuring high temperatures are known as **pyrometers.**

It has been found that a gas will not occupy any volume at a certain temperature. This temperature is known as absolute zero temperature. The temperatures measured with absolute zero as basis are called absolute temperatures. Absolute temperature is stated in degrees centigrade. The point of absolute temperature is found to occur at 273.15°C below the freezing point of water.Then: Absolute temperature = Thermometer reading in °C + 273.15. Absolute temperature is degree centigrade is known as degrees kelvin, denoted by K (SI unit).

ZEROTH LAW OF THERMODYNAMICS

'Zeroth law of thermodynamics' states that if two systems are each equal in temperature to a third, they are equal in temperature to each other.



Zeroth law of thermodynamics

THE THERMOMETER AND THERMOMETRIC PROPERTY

The zeroth law of thermodynamics provides the basis for the measurement of temperature. It enables us to compare temperatures of two bodies 1 and 2 with the help of a third body 3 and say that the temperature of 1 is the same as the temperature of 2 without actually bringing 1 and 2 in thermal contact. In practice, body3 in the zeroth law is called the **thermometer**. It is brought into thermal equilibrium with a set of standard temperature of a body 2, and is thus calibrated. Later, when any other body 1 is brought in thermal communication with the thermometer, we say that the body 1 has attained equality of temperature with the thermometer, and hence with body 2. This way, the body 1 has the temperature of body 2 given for example by, say the height of mercury column in the thermometer 3.

The height of mercury column in a thermometer, therefore, becomes a **thermometric property**. There are other methods of temperature measurement which utilize various other properties of materials, that are functions of temperature, as thermometric properties. Six different kinds of thermometers, and the names of the corresponding thermometric properties employed are given below:

Thermometer Thermometric property
1. Constant volumes gas Pressure (p)
2. Constant pressure gas Volume (V)
3. Alcohol or mercury-in-glass Length (L)
4. Electric resistance Resistance (R)
5. Thermocouple Electromotive force (E)
6. Radiation (pyrometer) Intensity of radiation (I or J)

Method in use before 1954:

Celsius and Fahrenheit scales are the two commonly used scales for the measurement of temperature. Symbols C and F are respectively used to denote the readings on these two scales. Until 1954 the temperature scales were based on two fixed points:

i) the steam point (boiling point of water at standard atmospheric pressure), and
ii) the ice point(freezing point of water).

The fixed points for these temperature scales are:

Temperature	Celsius scale	Fahrenheit scale
Steam point	100	212
Ice point	0	32
Interval	100	180

Method in use after 1954:

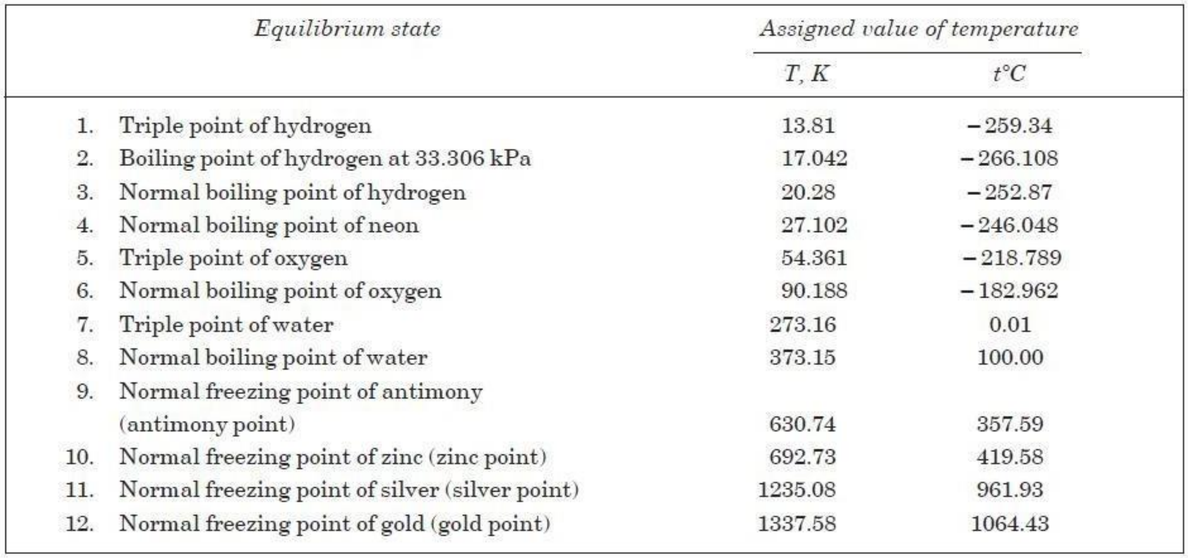
It was suggested by Kelvin that a single fixed point only was necessary to establish a temperature. He pointed out that *triple point of water* (the state at which ice, liquid water and water vapour coexist in equilibrium) could be used as the single point. The tenth CGPM, in 1954, adopted this fixed point, and value was set at 0.01°C or 273.16 K in the Kelvin scale thus established.

Correspondingly, the ice point of 0°C on the Celsius scale becomes equal to 273.15 K on the Kelvin scale. Celsius and Kelvin scales are distinguished by using distinct symbols *t* and *T,* the relation between these two is then given by:

$$T\ (K) = t\ (°C) + 273.15$$

The International Practical Temperature Scale

For the calibration of thermometric instruments the Seventh General Conference on Weight and Measures held in 1927 formulated a convenient scale known as the International Practical Temperature Scale. It was revised at Thirteenth General Conference in 1968. It consists of reproducible reference temperatures or primary fixed points defined by a number of pure substances with assigned values of temperatures determined with precision on ideal or perfect gas temperature scale as given in Table



Equilibrium state		Assigned value of temperature	
		T, K	*t°C*
1.	Triple point of hydrogen	13.81	−259.34
2.	Boiling point of hydrogen at 33.306 kPa	17.042	−266.108
3.	Normal boiling point of hydrogen	20.28	−252.87
4.	Normal boiling point of neon	27.102	−246.048
5.	Triple point of oxygen	54.361	−218.789
6.	Normal boiling point of oxygen	90.188	−182.962
7.	Triple point of water	273.16	0.01
8.	Normal boiling point of water	373.15	100.00
9.	Normal freezing point of antimony (antimony point)	630.74	357.59
10.	Normal freezing point of zinc (zinc point)	692.73	419.58
11.	Normal freezing point of silver (silver point)	1235.08	961.93
12.	Normal freezing point of gold (gold point)	1337.58	1064.43

Fixed Points of the International Practical Temperature Scale of 1968

Equilibrium state Assigned value of temperature It is stated here that :The triple point represents an equilibrium state between solid, liquid and vapour phases of a substance.

Normal boiling point is the temperature at which the substance boils at standard atmospheric pressure of 760 mm Hg. Normal freezing point is the solidification or the melting point temperature of the substance at standard atmospheric pressure. Based on the available method of measurement, the whole temperature scale may be divided into four ranges. The equations for interpolation for each range are as follows:

1.From – 259.34°C (triple point of hydrogen) to 0°C :

A platinum resistance thermometer of a standard design is used and a polynomial of the following form is fitted between the resistance of the wire Rt and temperature t

$$Rt = R0 (1 + At + Bt2 + Ct3)$$

where R0 = resistance at the ice point.

2. From 0°C to 630.74°C (Antimony point):

It is also based on platinum resistance thermometer. The diameter of the platinum wire must lie between 0.05 and 0.2 mm.

3. **From 630.74°C to 1064.43°C (Gold point) :**

It is based on standard platinum versus platinum-rhodium thermocouple. Following equation between e.m.f. E and temperature t is employed:

$$E = a + bt + ct$$

1) A temperature scale of certain thermometer is given by the relation $t = a \ln p + b$ Where a and b are constants and p is the thermometric property of the fluid in the thermometer. If at the ice point and steam point the thermometric properties are found to be 1.5 and 7.5 respectively what will be the temperature corresponding to the thermometric property of 3.5 on Celsius scale.

Solution. $t = a \ln p + b$ (Given) On Celsius scale :

Ice point = 0°C, and Steam point = 100°C

∴ From given conditions, we have $0 = a \ln 1.5 + b$ (i)

and $100 = a \ln 7.5 + b$ ...(ii)

i.e., $0 = a \times 0.4054 + b$ ...(iii)

and $100 = a \times 2.015 + b$ ...(iv)

Subtracting (iii) from (iv), we get $100 = 1.61a$

or $a = 62.112$

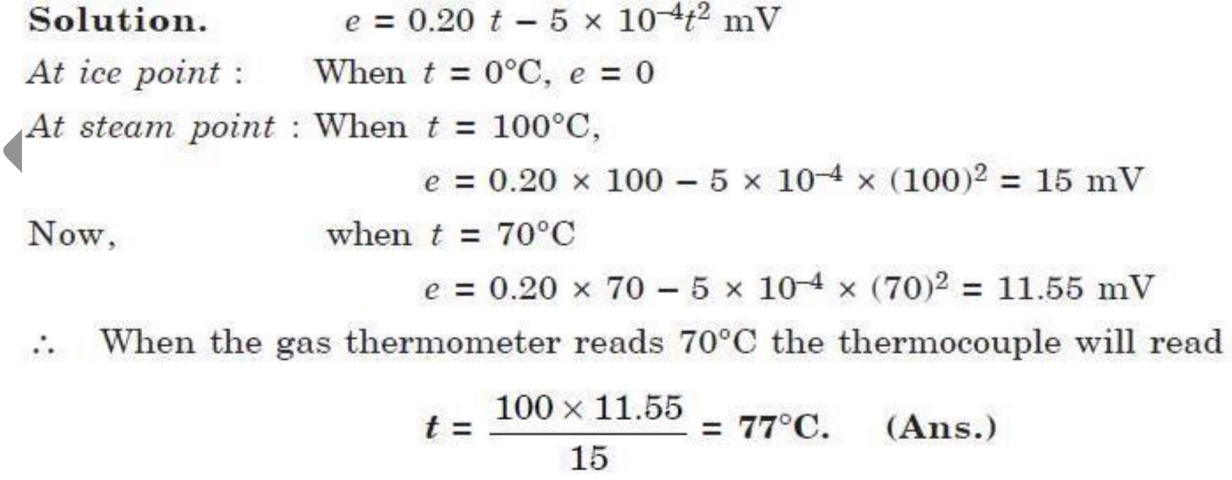
Substituting this value in eqn. (iii),

we get $b = – 0.4054 \times 62.112 = – 25.18$

∴ When $p = 3.5$ the value of temperature is given by

t = 62.112 ln (3.5) – 25.18= **52.63°C.**

2) A thermocouple with test junction at t°C on gas thermometer scale and reference junction at ice point gives the e.m.f. as e = 0.20 t – 5 × 10–4t2 mV. The milli voltmeter is calibrated at ice and steam points. What will be the reading on this thermometer where the gas thermometer reads 70°C?



Solution. $e = 0.20\ t - 5 \times 10^{-4} t^2$ mV

At ice point : When $t = 0°\text{C}$, $e = 0$

At steam point : When $t = 100°\text{C}$,

$$e = 0.20 \times 100 - 5 \times 10^{-4} \times (100)^2 = 15 \text{ mV}$$

Now, when $t = 70°\text{C}$

$$e = 0.20 \times 70 - 5 \times 10^{-4} \times (70)^2 = 11.55 \text{ mV}$$

∴ When the gas thermometer reads 70°C the thermocouple will read

$$t = \frac{100 \times 11.55}{15} = \mathbf{77°C.} \quad \textbf{(Ans.)}$$

WORK AND HEAT

Mechanics definition of work: Work is done when the point of application of a force moves in the direction of the force. The amount of work is equal to the product of the force and the distance through which the point of application moves in the direction of the force. i.e., work is identified only when a force moves its point of application through an observable distance.

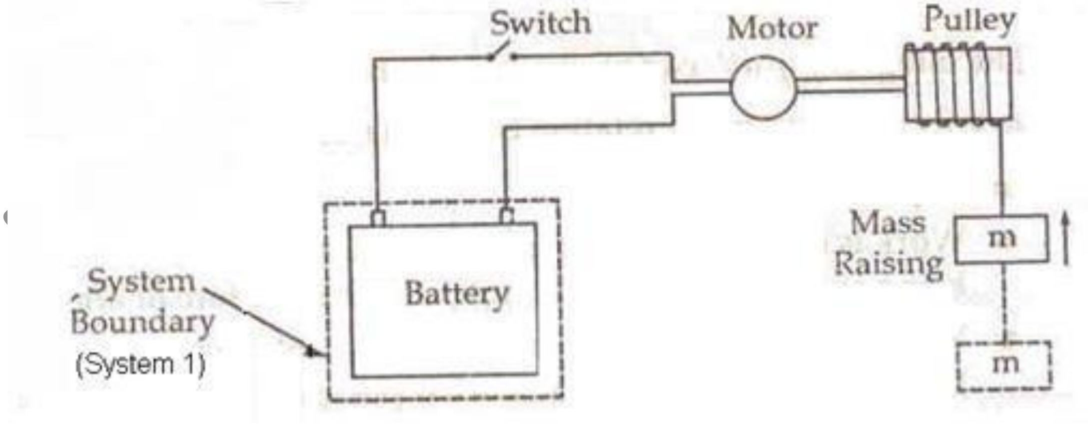
Mathematically, W = $\int_1^2 F.dx$

However, when treating thermodynamics from a macroscopic point of view, it is advantageous to tie in the definition work with the concepts of systems, properties and processes.

Thermodynamic definition of work: It is a kind of interaction that would occur at the system boundaries. It can be positive or negative. Definition of Positive work is said to be done by a system when the „sole effect‟ external to the system could be reduced to the raising of a weight.

Comments: The word „sole effect‟ indicates that the raising of weight should be the only interaction between the system and surroundings in order to say that there is work interaction between the system and the surroundings. The phrase „external to the system‟ indicates that the work is a boundary phenomenon. The magnitude of work interaction depends upon the system boundary. This is illustrated with an example.

Figure 1: Equivalence of Current Work Interaction between the System and the Surroundings



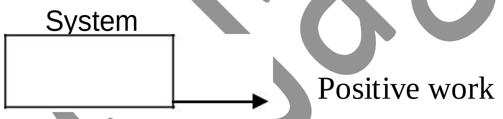
For the two systems shown in figure, system (1) comprising battery alone has work interaction with the surroundings, whereas for system (2) which includes motor, weights etc along with the battery, the work interaction is zero.

The word „could be reduced to" indicates that it is not necessary that weights should actually be raised in order to say that there is work interaction between the system and the surroundings. It is just sufficient to have an effect which is equivalent to the raising of weight.

Here an electrical storage battery constitutes system 1 whose terminals are connected to an electrical resistance coil through a switch. The circuit external to the battery constitutes the surroundings. When the switch is closed, the current flow through the coil, and the resistance (surroundings) become warmer and the charge of the battery (system) decreases. Obviously there has been interaction between the system and the surroundings. According to mechanics this interaction cannot be classified as work because their has been no action of force through a distance or of torque through an angle. However, as per thermodynamics concepts, the battery (system) does work as the electrical energy crosses the system boundary. Further, the electrical resistance can be replaced by an ideal frictionless motor pulley arrangement which can wind a string and thereby raise suspended weight. The sole effect, external to the system, is raising of a weight. As such interaction of battery with resistance coil is a work.

Sign Conventions for work:

Work is said to be positive, if it is done by the system on the surroundings



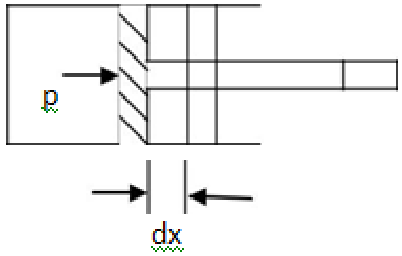
Work is said to be negative, if it is done on the system by the surroundings

Therefore, $W_{system} + W_{surroundings} = \text{Zero}$

The unit of work is N-m or Joule. The rate at which work is done by, or upon, the system is known as power. The unit of power is J/s or watt.

Work is one of the forms in which a system and its surroundings can interact with each other. There are various types of work transfer which can get involved between them.

Work done at the moving boundary of a system (Expression for displacement work)



Consider a piston-cylinder arrangement which contains certain working fluid undergoing quasi-static process.

Let p = Pressure exerted by the fluid on the piston

A = Area of c/s of the cylinder

dx = displacement of the piston when the system has undergone an infinitesimal change of state.

$\therefore$ Displacement work: dw = Force x displacement

= p.A x dx

i.e., dw = p.dV

Where dv is the infinitesimal change in volume of the system. If the system undergoes a finite change of state from state (1) to state (2).

Then the displacement work is given by

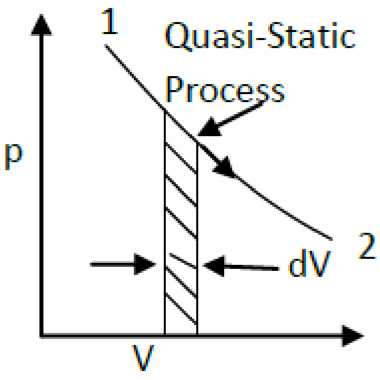
$$\int_1^2 dw = \int_1^2 p.dV$$

The integration of above equation can be done only if the relationship between P and v during the process is known i.e., if the path of the process is well defined. Hence, work is a path function. As work depends on the path of the process which it follows, there will be different values of work for different process between two given states. Hence the differentials of the path functions are in exact differentials. The symbol δ will be used to designate inexact differentials. The magnitude of the work transfer by the system during the process from state.

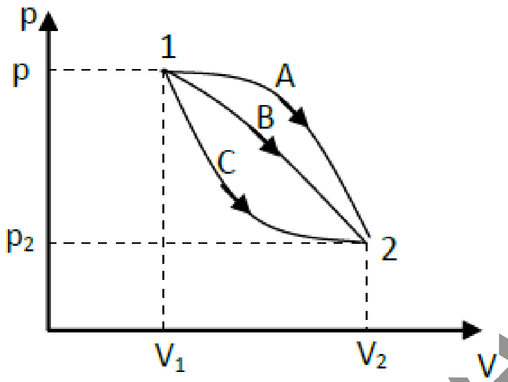
(1) to state (2) containing unit mass of the fluid will be written as, or

$$\int_1^2 \delta w = {}_1W_2 \text{ or } W_{1-2}.$$

The process can be represented by a full line on an appropriate thermodynamic coordinate system (in this case p-V diagram) and the area under the curve gives the work done by the system during the process.



Quasi-Static pdV work



Work-a path function

Inspection of the P V diagram above shows that just by specifying the end states 1 and 2 does not determine the area (or work); the nature of the curve needs to be known. The curve may be arched upwards or it may sag downwards, and the area under the curve will vary accordingly. For the same initial and final states, the work done by the system in following the paths A, B and C are different. Therefore the work is a path function and not a point function. Accordingly the work transfer across the system boundaries is not classified as a thermodynamic property.

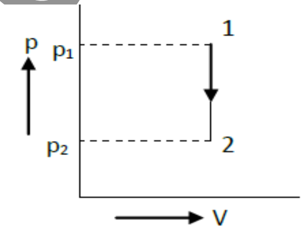
The expression w = pdV holds good under the following restrictions.

i) The system is closed
ii) There is no friction within the system
iii) The pressure and all other properties are the same on all the boundaries of the system
iv) The system is not influenced by motion, gravity, capillarity, electricity and magnetism

Expression for Displacement work for various Quasi-Static Processes (pdV work):

1) Constant volume process: **(Isochoric Process)**.

For a constant volume process i.e., V = constant (dV = 0) as represented in the p-V diagram below.

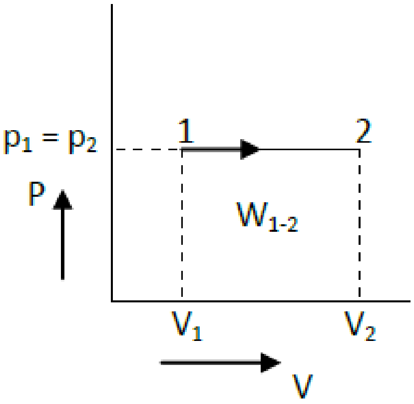


$W_{1\text{-}2} = \int_1^2 p.dV$ but $dV = 0$

$$\therefore \boxed{(W_d)_{1\text{-}2} = 0}$$

2) Constant pressure process: (Isobaric process).

For a closed system undergo a constant pressure process from state 1 (volume V_1 and pressure p_1) to a final state 2 (volume V_2). The process is represented in the p-V diagram as shown below.



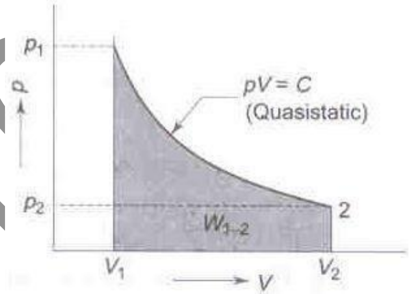
$$W_{1\text{-}2} = \int_1^2 p.dV, \text{ where } p = \text{constant}$$

$$\therefore\ W_{1\text{-}2} = p \int_1^2 dV$$

$$\therefore\ \boxed{(W_d)_{1\text{-}2} = p\,(V_2 - V_1)}$$

3) Hyperbolic process i.e., pV = constant:

The hyperbolic expansion process from state 1 to state 2 is represented on a p-V diagram as shown below.



Process in which pV = Constant

Process in which pV = Constant

$$W_{1\text{-}2} = \int_1^2 p.dV$$

But $pV = \text{constant}$ i.e., $pV = p_1V_1$, $\therefore\ p = \dfrac{p_1V_1}{V}$

$$\therefore W_{1\text{-}2} = \int_1^2 p.dV$$

$$= \int_1^2 \frac{p_1V_1}{V}.dV$$

$= p_1\ V_1\ [\ln V_2 - \ln V_1]$ where p_1 = Initial pressure of the system

V_1 = Initial volume of the system

p_2 = Final pressure of the system

V_2 = Final volume of the system

i.e., $(W_d)_{1\text{-}2} = p_1V_1 \ln\frac{V_2}{V_1}$

4) Polytropic process, i.e., pV^n = constant

A polytropic process is represented on a p-V diagram as shown below.

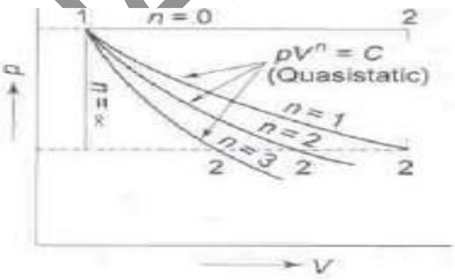


Figure: Process in which pV^n = Constant

$$W_{1\text{-}2} = \int_1^2 p.dV$$

But pV^n = constant i.e., $pV^n = p_1V_1^n = p_2V_2^n$

$$\therefore W_{1\text{-}2} = \int_1^2 \frac{p_1V_1^n}{V^n}.dV$$

$$= p_1\ V_1^n \int_1^2 V^{-n}.dV$$

$$= p_1\ V_1^n \left[\frac{V^{-n+1}}{-n+1}\right]_1^2$$

but $p_1V_1^n = p_2V_2^n$

$$= \frac{p_2V_2 - p_1V_1}{1-n}$$

$$\therefore (W_d)_{1-2} = \frac{p_1V_1 - p_2V_2}{n-1}$$

Where ‘n’ is called the index of expansion or compression

Note: 1. Work is a transient phenomenon i.e., it is present only during a process. Mathematically

speaking, work is a path function.

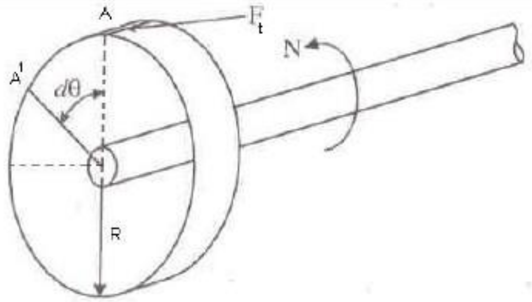
$$\therefore \int_1^2 dw = w_2 - w_1 \text{ is wrong}$$

$$= w_{1-2} \text{ i.e., } \delta w \text{ is inexact differentials.}$$

2. For irreversible process $\delta w \neq \int_1^2 P.dv$

Other Types of Work Transfer

1. Shaft Work:



Shaft work

Let F_t = Tangential force on the shaft

R = Radius of the shaft

$d\theta$ = Angular displacement of the shaft in an interval of time ‘dt’

$\therefore$ Shaft work in time interval ‘dt’, is $dW_s = F_t . AA^1$

$= F_t . R.d\theta$

i.e., $W_s = T.d\theta$

$\therefore$ Work done / unit time $= \frac{dW_s}{dt} = T . \frac{d\theta}{dt} = T.\omega$ where ω = angular velocity, T = Torque

But $\omega = \frac{2\pi N}{60}$ where N = rpm of the shaft

$$\text{Shaft work, } W_S = \frac{2\pi NT}{60} \text{ watts}$$

2. Stirring Work: Stirring work is nothing but shaft work is done on the system by using a stirrer which is driven by a shaft.

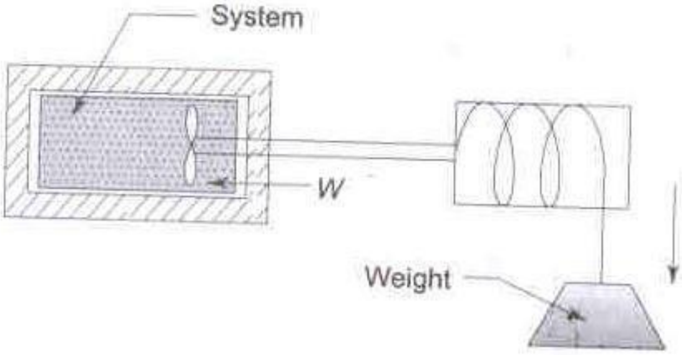


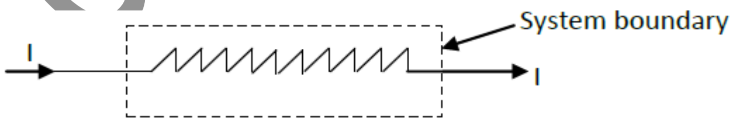
Figure: Paddle-wheel work

As the weight is lowered, and the paddle wheel turns, there is work transfer into the system which gets stirred. Since the volume of the system remains constant, $\int$ pdv = 0. If m is the mass of the weight lowered through a distance dz and T is the torque transmitted by the shaft in rotating through an angle dθ , the differential work transfer to the fluid is given by

$$\delta w = mgdz = Td\theta$$

and the total work transfer is $w = \int_1^2 mgdz = \int_1^2 W^1 dz = \int_1^2 Td\theta$ where W^1 is the weight lowered

3. Electrical Work: When a current flows through a resistor, taken as system, there is work transfer into the system. This is because the current can drive a motor, the motor can drive a pulley and the pulley can raise a weight.



The current I, flows is given by,

$$I = \frac{dC}{d\tau} \quad \text{where } C = \text{charge in coulombs}$$

$$\tau = \text{time in seconds}$$

Thus dC is the charge crossing a system boundary during time $d\tau$. If E is the voltage potential, the work is $\delta w = E.dC$

$$= EI\, d\tau$$

$$\therefore\ w = \int_1^2 EI\, d\tau$$

$\therefore$ The electrical work is, $w = \lim\limits_{\delta\tau \longrightarrow 0} \dfrac{dw}{d\tau} = EI$

This is the rate at which work is transferred.

4. Work done in stretching a wire: Consider a wire as the system. If the length of the wire in which there is a tension Ŧ is changed from L to L + dL, the infinitesimal amount of work that is done is equal to, w = - Ŧ dL

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

For a finite change of length, $w = \int_1^2$ Ŧ dL

Within the elastic limits, if E is the modulus of the elasticity, is the stress, ε is the strain, and A is the cross sectional area, then

Ŧ = A = E.ε.A

Therefore w = - E.ε.AdL

But dε = dL/L or dL = L x dε

w = - Ŧ dL = - E.ε.A. L dε

i.e., $w = -EAL \int_1^2 \varepsilon\, d\, \varepsilon$

5. Work done in changing the area of a surface film: A film on the surface of a liquid has a surface tension which is a property of the liquid and the surroundings. The surface tension acts to make the surface area of the liquid a minimum. It has the unit of force per unit length.

The work done on a homogeneous liquid film in changing its surface area by an infinitesimal amount dA is

$\delta w = -\,\sigma\, dA$ when $\sigma \models$ surface tension (N/m)

$$\therefore\ w = -\int_1^2 \sigma\, dA$$

6. Magnetization of a paramagnetic field: The work done per unit volume on a magnetic material through which the magnetic and magnetization fields are uniform is,

$$\delta w = -\ H.dI$$

i.e., $w = -\ \int_1^2 H.dI$

Where H = field strength

I = Component of the magnetization field in the direction of the field.

-ve sign provides that an increase in magnetization (+ve dI) involves -ve work.

Note: It may be noted in the above expressions that the work is equal to the integral of the product of an intensive property and the change in its related extensive property. These expressions are valid only for infinitesimally slow quasi-static process.

Network Transfer: The network interaction between the system and the surroundings for any process will be the algebraic sum of all types of work interaction that has taken place between the system and the surroundings.

Heat: Heat is a mode of energy transfer that takes place between the system and the surroundings solely due to the temperature difference. Thus, heat is a transient phenomenon. It can be recognized only during a process. It is not a thermodynamic property of the system. Like work, heat is a path function i.e., the magnitude of heat transfer between the system and surroundings depends upon the type of process the system is undergoing.

Heat transfer always takes place from a region of higher temperature to a region of low temperature. The magnitude of the heat transfer into unit mass of the fluid in the system during a process from state (1) to state (2) will be written as $\int_1^2 \delta q = {}_1q_2 \ or \ q_{1-2}$ and not as $\int_1^2 \delta q = q_1 - q_2$

$\int_1^2 \delta q$ represents the total heat transfer that takes place when the system undergoes a change of state from state 1 to state 2.

Sign Convention:

Heat transfer is considered as positive if it takes place from the surroundings to the system and it is considered as negative if it takes place from the system to the surroundings.

During an adiabatic process, Q = 0

Units: Since heat is a form of energy transfer it will have the same units as that of energy. In SI units it is expressed in Joules (J) or Kilo Joules (kJ).

Comparison between work and heat:

Similarities:

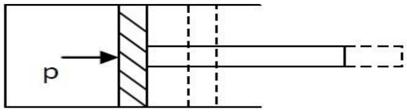
- Both are path functions and inexact differentials.
- Both are boundary phenomenon i.e., both are recognized at the boundaries of the system as they cross them.
- Both represent transient phenomenon; these energy interactions occur only when a system undergoes change of state i.e., both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
- A system possesses energy, but not work or heat.
- Concepts of heat and work are associated not with a store but with a process.

Dissimilarities:

- Heat is energy interaction due to temperature difference only; work is by reasons other than temperature difference.
- In a stable system, there cannot be work transfer; however there is no restriction for the transfer of heat.
- The sole effect external to the system could be reduced to rise of a weight but in the case of a heat transfer other effects are also observed.
- Heat is low grade energy whereas work is a high grade energy

1. A gas system, confined by a piston and cylinder, undergoes a change of state such that the product of pressure and volume remains constant. If the process begins at a pressure of 3 bar and a volume 0.015m^3 and proceeds until the pressure falls to half its initial value, determine the magnitude and direction of the work flow.

Solution:



pV = C i.e., hyperbolic process or $p_1 V_1 = p_2 V_2$

Given, $p_1 = 3 \times 10^5$ Pa $\quad V_1 = 0.015\ m^3 \quad p_2 = 1.5 \times 10^5\ m^3$

$V_2 = ? \quad W_{1-2} = ?$

We have, $p_1V_1 = p_2 V_2 \qquad \therefore\ V_2 = \frac{p_1V_1}{p_2} = \frac{3x10^5 x0.015}{1.5x10^5} = 0.03\ m^3$

$$\therefore \text{Displacement work, } (W_d)_{1-2} = \int_1^2 p.dV = p_1V_1 \ln \frac{V_2}{V_1}$$

$$= 3119.16\ J \qquad = 3.1192\ kJ$$

Positive sign indicates work is done by the system on the surroundings.

2. A certain amount of gas is compressed from 1 bar and $0.1m^3$ to 5 bar and $0.03m^3$. The process is according to the law $pV^n = K$. Determine the magnitude and direction of work.

Solution: Given: p_1 = 1 bar; $V_1 = 0.1\ m^3$; p_2 = 5 bar; $V_2 = 0.03$

We have for a polytropic process,

Displacement work, = $(W_d)_{1-2} = \frac{p_1V_1 - p_2V_2}{n - 1}$

To find the compression index n, we have,

$$p_1V_1^n = p_2V_2^n = C$$

$$\text{i.e., } \frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^n$$

Taking log's on both sides we have

$$\ln \frac{p_1}{p_2} = n.\ln \frac{V_2}{V_1}$$

$$\therefore n = \frac{\ln \frac{1}{5}}{\ln \frac{0.03}{0.1}} = 1.34$$

i.e., work done on the gas = 14.706 kJ

3. A gas confined in a cylinder by a piston is at pressure of 3 bar and a volume of 0.015 m^3. The final pressure is 1.5 bar. Determine the magnitude and direction of work transfer for the following

processes. i) $p \alpha V$, ii) $p \alpha \frac{1}{V}$, iii) $p \alpha V^2$ and iv) $p \alpha \frac{1}{V^2}$

Solution: Given: $p_1 = 3 \times 10^5$ Pa; $V_1 = 0.015$ m^3; $p_2 = 1.5 \times 10^5$ Pa $V_2 = ?$ $(W_d) = ?$

i) $p \alpha V$ i.e., $\frac{p}{V} = \frac{p_1}{V_1} = C = \frac{p_2}{V_2}$

We have, $(W_d)_{1\text{-}2} = \int_1^2 p.dV$

$$= \int_1^2 \frac{p_1 V}{V_1}.dV = \frac{p_1}{V_1} \int_1^2 V.dV$$

we have $\frac{p_1}{V_1} = \frac{p_2}{V_2}$

$$\therefore (W_d)_{1\text{-}2} = \frac{3x10^5}{2x0.015}[0.0075^2 - 0.015]^2 = -1.688 \text{ kJ}$$

-ve sign indicates that work is done on the system

ii) $p \alpha \frac{1}{V}$ i.e., $pV = C$

Ans: $(W_d)_{1\text{-}2} = 3.1192$ kJ

iii) $p \alpha V^2$ i.e., $\frac{p_1}{V_1^2} = \frac{p_2}{V_2^2} = C = \frac{p}{V^2}$ $\therefore V_2 = \sqrt{\frac{p_2 - V_1^2}{p_1}} = 0.0106$ m^3

$(W_d)_{1\text{-}2} = \int_1^2 p.dV$

$$= \int_1^2 \frac{p_1}{V_1^2} V^2.dV$$

$$= \frac{p_1}{V_1^2} \int_1^2 V^2.dV$$

= -0.9707 kJ

-ve sign indicates that work is done on the system

iv) $p \alpha \frac{1}{V^2}$ i.e., $pV^2 = C = p_1V_1^2 = p_2V_2^2$

$$\therefore V_2 = \sqrt{\frac{p_1V_1^2}{p_2}} = \sqrt{\frac{3x0.015^2}{1.5}} = 0.0212\ m^3$$

$$\text{We have } (W_d)_{1\text{-}2} = \int_1^2 p.dV = \int_1^2 \frac{p_1V_1^2}{V^2}.dV \quad = p_1V_1^2 \int_1^2 \frac{1}{V^2}.dV$$

$$= p_1V_1^2\left[-\frac{1}{V}\right]_1^2$$

$$= p_1V_1^2\left(-\frac{1}{V_2}+\frac{1}{V_1}\right)$$

$$= p_1V_1^2\left(\frac{1}{V_1}-\frac{1}{V_2}\right)$$

Substituting the given values, we get $(W_d)_{1\text{-}2}$ = 1.316 kJ

+ve sign indicates that work is done by the system

4. The average heat transfer from a person to the surroundings when he is not actively working is about 950 kJ/hr. suppose that in the auditorium containing 1000 people the ventilation system fails. a) How much does the internal energy of air in the auditorium increase during the first 15 minutes after the ventilation fails? b) Considering the auditorium and all the people as system and assuming no heat transfer. to surroundings, how much does the int. energy of the system change? How do you account for the fact that the temperature of air increases?

Solution: a) Average heat transfer per person = 960 kJ/hr

= 960 / 60 = 15.83 kJ /min

∴ Average heat transfer / person for 15 min = 237.5 kJ

∴ Average heat transfer for 15 min in the auditorium containing 1000 people

$$Q = 237.5 \text{ x } 1000 = 237500 \text{ kJ/min}$$

From first law of TD, we have $Q = \Delta E + W$

$$237500 = \Delta E + 0$$

$$\therefore \Delta E = 237.5 \text{ MJ}$$

MODULE-2

FIRST LAW OF THERMODYNAMICS

First Law of Thermodynamics to open system:

In the case of closed system there is only energy transfer across the system boundary. But in many engineering applications we come across open systems where in both mass and energy transfer takes place. The energies that cross the system boundary are as follows.

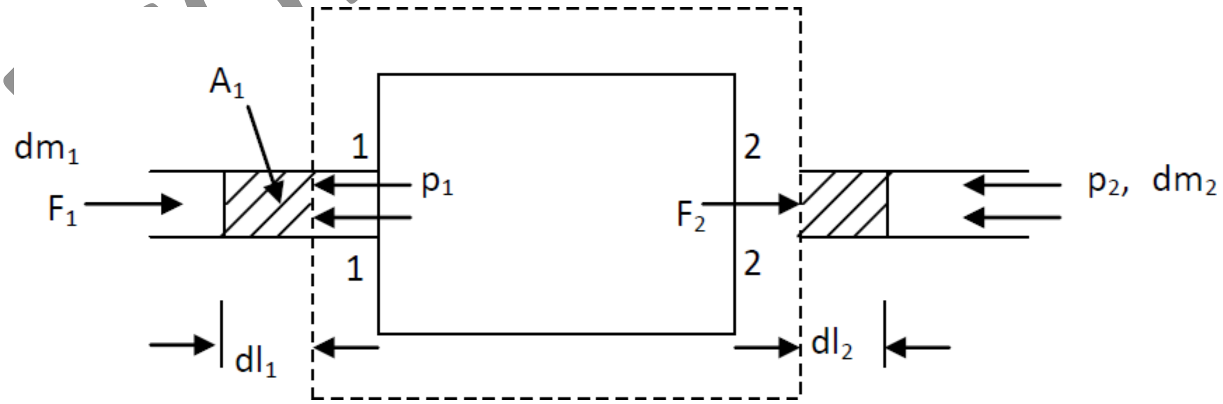
1) **Internal energy**: Each kg of matter has the internal energy „u‟ and as the matter crosses the system boundary the energy of the system changes by „u‟ for every kg mass of the matter that crosses the system boundary.

2) **Kinetic energy**: Since the matter that crosses the system boundary will have some velocity say$V$ each kg of matter carries a k.E. $V^2 / 2$ thus causing the energy of the system to change by this amount for every kg of matter entering the system boundary.

3) **Potential energy**: P.E. is measured with reference to some base. Thus „Z‟ is the elevation of the matter that is crossing the system boundary, then each kg of matter will possess a P.E. of gZ.

4) **Flow energy or Flow work**: This energy is not directly associated with the matter crossing the system boundary. But it is associated with the fact that there must be some pumping process which is responsible for the movement of the matter across the system boundary. Thus external to the system there must be some force which forces the matter across the system boundary and the energy associated with this is called flow energy.

Flow Work: Consider a flow process in which a fluid of mass dm_1 is pushed into the system at section 1 and a mass dm_2 is forced out of the system at section 2 as shown in fig.



In order to force the fluid to flow across the boundary of the system against a pressure p_1, work is done on the boundary of the system. The amount of work done is $\delta W = - F_1.dl_1$,

Where F_1 is the force and dl_1 is the infinitesimal displacement, but $F_1 = p_1A_1$

$\therefore \delta W = - p_1A_1\, dl_1 = - p_1dv_1$

i.e., the flow work at section 1 = $- p_1v_1$

Similarly, the work done by the system to force the fluid out of the system at section 2 = $+ p_2v_2$

Hence net flow work = $p_2V_2 – p_1V_1$

For unit mass, the flow work is ($p_2V_2 – p_1V_1$). Flow work is expressed entirely in terms properties of the system. The net flow work depends out on the end state of the fluid and it is a thermodynamics property. Also the fluid contains energies like internal energy, potential energy and due to the motion of the fluid, kinetic energy, in addition to the flow work. When a fluid enters an open system, these properties will be carried into the system. Similarly when the fluid leaves the system, it carries these energies out of the system. Thus in an open system, there is a change in energy of the system.

5. **Control Volume**: The first and most important step in the analysis of an open system is to imagine a certain region enclosing the system. This region having imaginary boundary is called control volume, which can be defined as follows. A C.V. is any volume of fixed shape, and of fixed position and orientation relative to the observer. Across the boundaries of the C.V. apart from mass flow, energy transfer in the form of heat and work can take place just as similar to the energy transfer across the boundaries of a system.

Thus the difference between C.V. and system are

i) The system boundary may and usually does change shape, position, orientation relative to the observer. The C.V. does not by definition.

ii) Matter may and usually does flow across the system boundary of the C.V. No such flow takes place across the system boundary by definition.

First law of thermodynamics for an open system (Flow process):

We have 1st law of thermodynamics to a closed system as,

$$\delta Q – \delta W = dU + d(KE) + d\,(PE)$$

$$= d\,[E]$$

$$dm_1\left[p_1v_1+u_1+\frac{V_1^2}{2}+gZ_1\right]$$

$$dm_2\left[p_2v_2+u_2+\frac{V_2^2}{2}+gZ_2\right]$$

The flow process is shown in fig. This analysis can be expressed mathematically as,

$$\delta Q-\delta W+dm_1\left[p_1v_1+u_1+\frac{V_1^2}{2}+gZ_1\right]$$

Where state (1) is the entering condition and state (2) is the leaving condition of the fluid. This is a general equation of the first law of thermodynamics applied to open system.

Note: The equation is valid to both open and closed system. For closed system, $dm_1=0$ & $dm_2=0$

Energy Equation for open system: The general form of first law of thermodynamics applied to an open system is called steady-flow energy equation (SFEE) i.e., the rate at which the fluid flows through the C.V. is constant or steady flow. SFEE is developed on the basis of the following assumptions.

i) The mass flow rate through the C.V. is constant, i.e., mass entering the C.V. / unit time = mass leaving the C.V. /unit time. This implies that mass within the C.V. does not change.

ii) The state and energy of a fluid at the entrance and exit do not vary with time, i.e., there is no change in energy within the C.V.

iii) The rates of heat and work transfer into or out of the C.V. do not vary with time.

For a steady flow process, $m=m_1=m_2$ & $d(E)_0=0$ as $Q\neq f(T)$ & $W\neq f(T)$

SFEE on the basis unit mass:

Energy entering to the system = energy leaving the system

$$\text{i.e., }\left[u_1+p_1v_1+\frac{V_1^2}{2}+gZ_1\right]+Q \qquad =W+\left[u_2+p_2v_2+\frac{V_2^2}{2}+gZ_2\right]$$

$$\text{or }\left[h_1+\frac{V_1^2}{2}+gZ_1\right]+Q=W\left[h_2+\frac{V_2^2}{2}+gZ_2\right]$$

$$=\Delta\left[h+\frac{V^2}{2}+gZ_2\right]$$

Where Q = heat transfer across the C.V, W = shaft work across the C.V, h = Enthalpy,
V = velocity, Z = elevation and g = gravitational acceleration

Displacement work for a flow process (open system):

From SFEE, when changes in kinetic & potential energies are neglected, $\delta q - \delta W = dh$

Or $\delta W = \delta q - dh$ --- (1)

From the 1st law of thermodynamics, we have $\delta q - \delta W = du$

For a rev. process, $\delta W = Pdv$

$\delta q = du + Pdv$

Also, from the definition of enthalpy, $h = u + pv$

Or $dh = du + d(pv)$

Sub δq & dh in equation (i)

$\delta W = [du + p.dv] - [du + d(pv)]$

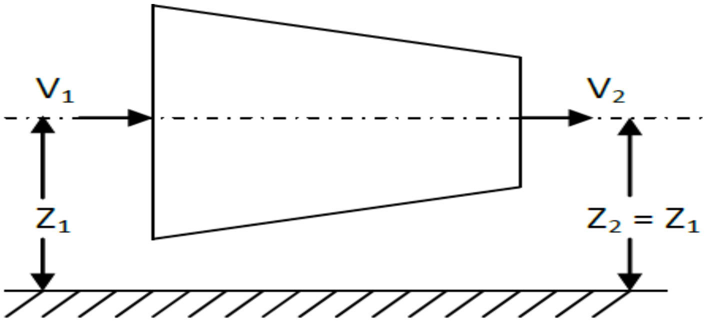
$= p.dv - p.dv - v.dp$

$W = -vdp$

Note: With negligible PE & KE, for a non-flow rev. process, the work interaction is equal to $\int_1^2 p.dv$ where as for a steady-flow rev. process, it is equal to $-\int_1^2 vdp$

Application of SFEE:

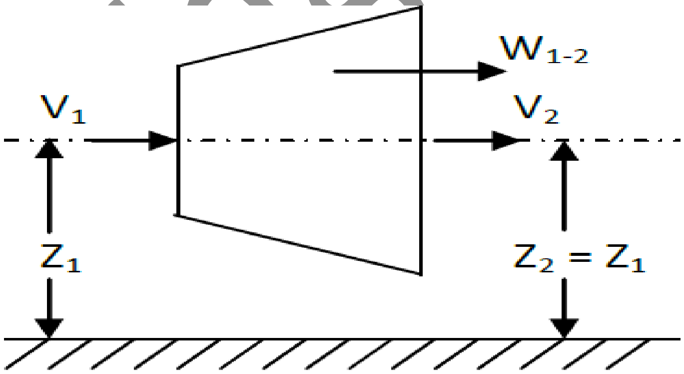
i) Nozzle and Diffuser: Nozzle is a duct of varying c/s area in which the velocity increases with a corresponding drop in pressure. Since the flow through the nozzle occurs at a very high speed, there is hardly any time for a fluid to gain or loose heat and hence flow of the fluid is assumed to be adiabatic. And also there is no work interaction during the process, i.e., $W_s = 0$, $Q = 0$, $Z_1 = Z_2$



We have from SFEE, $Q - W = \Delta h + \Delta PE + \Delta KE$

$$0 = h_2 - h_1 + \frac{V_2^2 - V_1^2}{2}$$

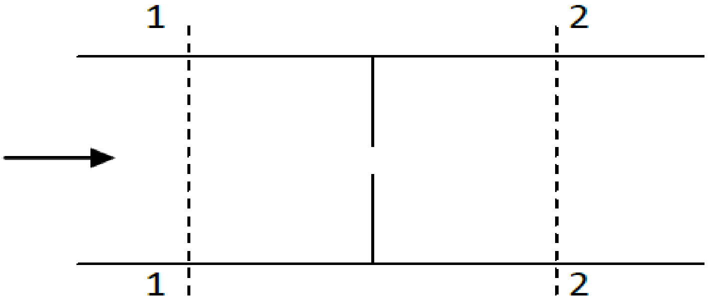
Turbine and Compressor (rotary): Turbine is a device which produces work by expanding a high pressure fluid to a low pressure. The fluid is first accelerated in a set of nozzle and then directed through curved moving blades which are fixed on the rotor shaft. The direction of the fluid changes which it flows through the moving blades, due to which there is a change in momentum and a force exerted on the blades producing torque on the rotor shaft. Since the velocity of flow of the fluid through the turbine is very high, the flow process is generally assumed to be adiabatic, hence heat transfer q = 0. The change in PE is neglected as it is negligible.



$\therefore$ SFEE is $\qquad W_{1\text{-}2} = (h_1 - h_2) - ½ (V_2^2 - V_1^2)$

Compressor is a device in which work is done on the fluid to raise its pressure. A rotary compressor can be regarded as a reversed turbine. Since work is done on the system, the rate of work in the above equation is negative and the enthalpy after compression h_2 will be greater than the enthalpy before compression h_1.

iii) **Throttling Process**: When a fluid steadily through restricted passages like a partially closed valve, orifice, porous plug etc., the pressure of the fluid drops substantially and the process is called throttling. In a throttling process, expansion of the fluid takes place so rapidly that no heat transfer is possible between the system and the surroundings. Hence the process is assumed to occur adiabatically. The work transfer in this process is zero.



SFEE is $Q_{1\text{-}2} - W_{1\text{-}2} = \Delta h + \Delta KE + \Delta PE$

We have, $Q = 0$; $W = 0$; $Z_1 \cong Z_2$, $V_1 \cong V_2$

i.e., $h_1 = h_2$

In a throttling process, the enthalpy remains constant. The throttling process is irreversible because when a fluid is throttled, it passes through a series of non-equilibrium states.

iii) **Heat Exchanger**: A heat exchanger is a device in which heat is transferred from one fluid to another. It is used to add or reduced heat energy of the fluid flowing through the device. Radiator in an automobile, condenser in a steam power and refrigeration plants, evaporator in a refrigerator are examples of heat exchangers. There will be no work interaction during the flow of the fluid through any heat exchanger.

Eg: i) <u>Steam condenser</u>: Used to condense the steam. It a device in which steam loses heat as it passes over the tubes through which water is flowing.

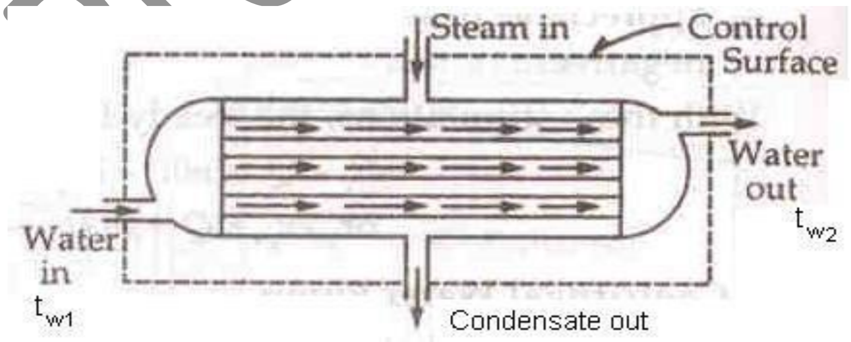


Figure: Heat Exchanger

We have KE = 0, PE = 0 (as their values are very small compared to enthalpies)

W = 0 (since neither any work is developed nor absorbed)

SFEE is $Q = h_2 - h_1$

$\therefore$ i.e., $h_1 - Q = h_2$ --- (1)

Where Q = heat lost by 1 kg of steam passing through the condenser.

Assuming there are no other heat interactions except the heat transfer between steam and water, then Q = heat gained by water passing through the condenser.

Substituting Q in the above equation (1),

$$h_2 - h_1 = m_w C_w (T_{w2} - T_{w1})$$

Where m_w = mass of cooling water passing through the condenser

C_w = specific heat of water

In a condenser there are 2 steady flow streams namely (i) Vapour that losses heat (ii) The coolant (water) that receives heat.

Let m_w = mass flow rate of coolant

m_s = mass flow rate of steam

h_{1w} = Enthalpy-coolant entry

h_{1s} = Enthalpy-steam entry

h_{2w}, h_{2s} = Enthalpy of coolant, steam at exit

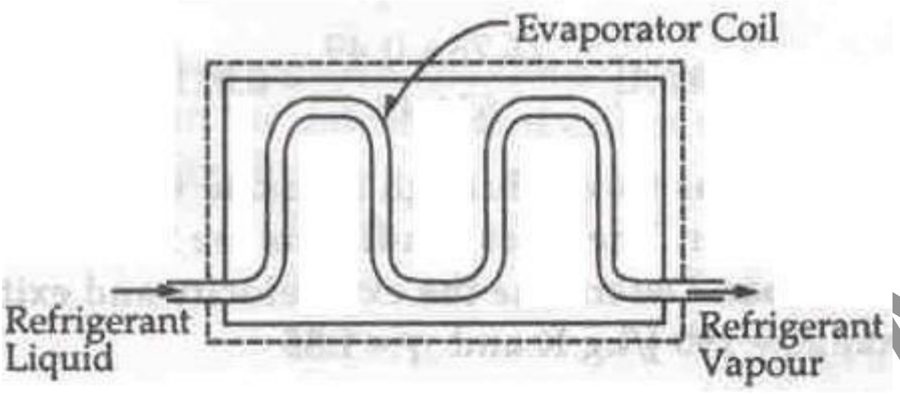
$$m_w h_{1w} + m_s h_{1s} = m_w h_{2w} + m_s h_{2s}$$

ii) Evaporator: An evaporator is a component of a refrigeration system and is used to extract heat from the chamber which is to be kept at low temperature. The refrigerating liquid enters the evaporator, absorbs latent heat from the chamber at constant pressure and comes out as a vapour. SFEE is

$$\dot{m}\, h_1 + \dot{Q} = \dot{m}\, h_2 \quad \text{Since } \dot{W} = 0,\ \Delta KE = \Delta PE = 0$$

$$\therefore \dot{Q} = \dot{m}\,(h_2 - h_1)$$

Q is taken as positive because heat flows from the chamber to the evaporator coil.



iv) **Boiler**: It is an equipment used for the generation of the steam. Thermal energy released by combustion of fuel is transferred to water which vaporizes and gets converted into steam at the desired pressure and temperature. The steam thus generated is used for

- Producing mechanical work by expanding it in steam engine or steam turbine.
- Heating the residential and industrial buildings in cold weather and
- Performing certain processes in the sugar mills, chemical and textile industries.

Velocity change is negligible $V_1 = V_2$

Change in elevation is also negligible $Z_2 = Z_1$

Work done = 0

$\therefore$ SFEE is $h_1 + q = h_2$

$\therefore$ $q = h_2 - h_1$

$= (u_2 - u_1) + (p_2 v_2 - p_1 v_1)$

First law of thermodynamics for a closed system undergoing a cyclic process

"When a system undergoes a thermodynamic cyclic process, then the net heat supplied to the system from the surroundings is equal to the net work done by the system on its surrounding".

i.e., $\oint \delta Q = \oint \delta W$ where $\oint$ represents the sum for a complete cycle.

The first law of thermodynamics cannot be proved analytically, but experimental evidence has repeatedly confirms its validity and since no phenomenon has been shown to contradict it, therefore the first law is accepted as a law of nature

Joule's Experiment:

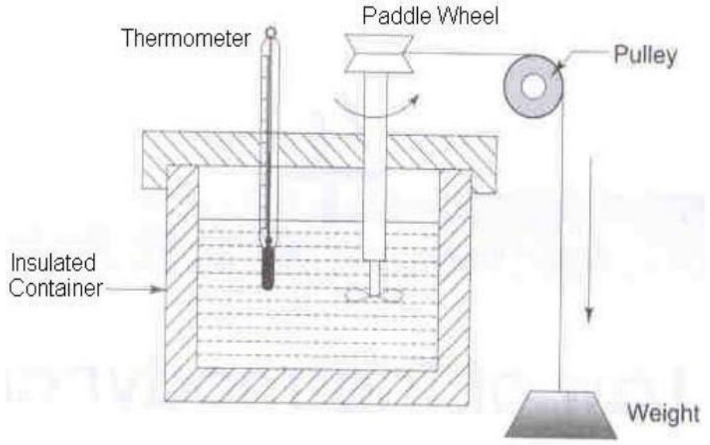


Figure: Joule‟s Experiment

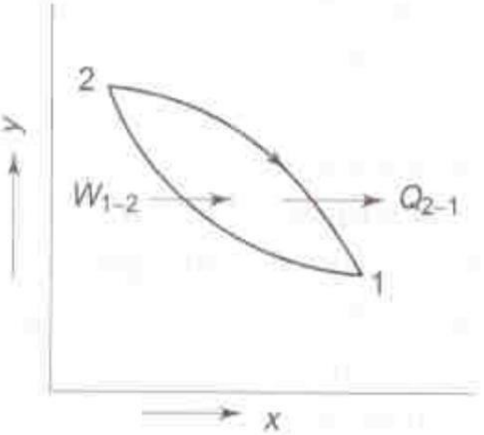


Figure: Cycle completed by a system with two energy interactions i.e., work transfer followed by heat transfer

Figure shows the experiment for checking the first law of thermodynamics. The work input to the paddle wheel is measured by the fall of weight, while the corresponding temperature rise of liquid in the insulated container is measured by the thermometer.

The process 1-2 undergone by the system is shown in figure i.e., W_{1-2}. Let the insulation be removed. The system and the surrounding interact by heat transfer till the system returns to its original temperature, attaining the condition of thermal equilibrium with the atmosphere. The amount of heat transfer Q_{2-1} from the system during this process 2-1 is shown in figure. The system thus executes a cycle, which consists of a definite amount of work input W_{1-2} to the system followed by the transfer of an amount of heat Q_{2-1} from the system.

Joule carried out many such experiments with different type of work interactions in a variety of systems, he found that the net work input the fluid system was always proportional to the net heat transferred from the system regardless of work interaction. Based on this experimental evidence Joule stated that,

"When a system (closed system) is undergoing a cyclic process, the net heat transfer to the system is directly proportional to the net work done by the system". This statement is referred to as the first law for a closed system undergoing a cyclic process.

$$\text{i.e., } \oint \delta Q \ \alpha \ \oint \delta W$$

If both heat transfer and work transfer are expressed in same units as in the S.I. units then the constant of proportionality in the above equation will be unity and hence the mathematical form of first law for a system undergoing a cyclic process can be written as

$$\text{i.e.,} \oint \delta Q \ \alpha \oint \delta W$$

If the cycle involves many more heat and work quantities as shown in figure, the same result will be found.

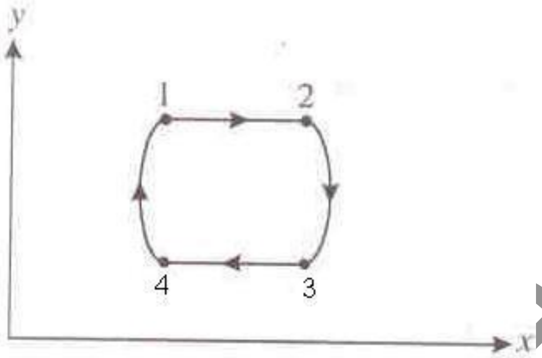


Figure: Cyclic Process on a Property Diagram

For this cyclic process the statement of first law can be written as

$$\oint_{1-2-3-4-1} \delta Q = \oint_{1-2-3-4-1} \delta W$$

The cyclic integral in the above equation can be split into a series of non cyclic integral as

$$\int_1^2 \delta Q + \int_2^3 \delta Q + \int_3^4 \delta Q + \int_4^1 \delta Q = \int_1^2 \delta W + \int_2^3 \delta W + \int_3^4 \delta W + \int_4^1 \delta W$$

or ${}_1Q_2 + {}_2Q_3 + {}_3Q_4 + {}_4Q_1 = {}_1W_2 + {}_2W_3 + {}_3W_4 + {}_4W_1$

i.e., $\oint \delta Q = \oint \delta W$

or $(\sum Q)_{\text{cycle}} = (\sum W)_{\text{cycle}}$

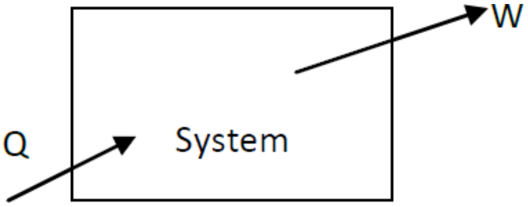
This is the first law for a closed system undergoing a cyclic process. i.e., it is stated as

"When a closed system is undergoing a cyclic process the algebraic sum of heat transfers is equal to the algebraic sum of the work transfers".

First law for a closed system undergoing a non-cyclic process (i.e., for a change of state):

If a system undergoes a change of state during which both heat transfer and work transfer are involved, the net energy transfer will be stored or accumulated within the system.

If Q is the amount of heat transferred to the system and W is the amount of work transferred from the system during the process as shown in figure,

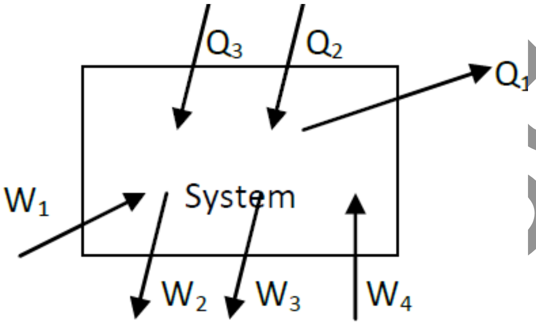


The net energy transfer (Q-W) will be stored in the system. Energy in storage is neither heat or work and is given the name internal energy or simply, the energy of the system.

$$Q - W = \Delta E$$

$$\text{or } Q = \Delta E + W$$

If there are more energy transfer quantities involved in the process as shown in figure.



First law gives

$$(Q_2 + Q_3 - Q_1) = \Delta E + (W_2 + W_3 - W_1 - W_4)$$

i.e., energy is thus conserved in the operation. Therefore the first law is a particular formulation of the principle of the conservation of energy. It can be shown that the energy has a definite value at every state of a system and is therefore, a property of a system.

Energy – A property of the system:

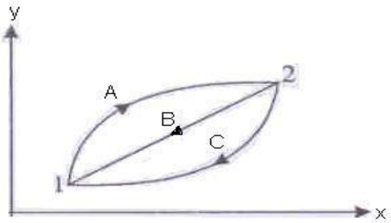


Figure: First law to a non cyclic process

Consider a system that undergoes a cycle, changing from state 1 to state 2 by process A and returning from state 2 to state 1 by process B.

We have from 1st law of thermodynamics, $\oint \delta Q = \oint \delta W$

For the process, 1-A-2-B-1, $\oint\limits_{1-A-2-B-1} \delta Q = \oint\limits_{1-A-2-B-1} \delta W$

Considering the two separate processes, we have

$$ {}_A\int_1^2 \delta Q + {}_B\int_2^1 \delta Q = {}_A\int_1^2 \delta W + {}_B\int_2^1 \delta W \qquad \text{--- (1)}$$

Now consider another cycle, the system changing from state 1 to state 2 by process A, as before and returning to state 1 by process C. For this cycle we can write

$$ {}_A\int_1^2 \delta Q + {}_C\int_2^1 \delta Q = {}_A\int_1^2 \delta W + {}_C\int_2^1 \delta W \qquad \text{--- (2)}$$

Subtracting (2) from (1), we get

$$ {}_B\int_2^1 \delta Q - {}_C\int_2^1 \delta Q = {}_B\int_2^1 \delta W + {}_C\int_2^1 \delta W $$

Since B and C represent arbitrary processes between state 1 to state 2, we conclude that the quantity (Q - W) is the same for all processes between state 1 and state 2. (Q - W) depends only on the initial and final states and not on the path followed between the two states. This is a point function and differential is a property of the system. This property is called the energy of the system, E. Therefore, we can write

$Q - W = dE$

Or $\delta Q = dE + \delta W$

If it is integrated between initial and final states, 1 and 2, we get

$Q_{1-2} = E_2 – E_1 + W_{1-2}$

i.e., $Q_{1-2} - W_{1-2} = E_2 – E_1$

The above equation is the statement of first law for a closed system undergoing a non cyclic process, where Q_{1-2} represents the net heat transfer between the system and the surroundings during the process, W_{1-2} represents net work transfer between the system and the surroundings during the process and $(E_2 – E_1)$ represents the change in the energy of the system during the process.

Classification of Energy of the System:

The energy E is an extensive property and the specific energy e = E/m (J/kg) is an intensive property. Energy E represents the total energy of the system.

i.e., E = kinetic energy (KE) + Potential Energy (PE) + remaining forms of energy.

Since K.E and P.E are macroscopic quantities and can be measured very easily and so they are considered separately in thermodynamics. The remaining energies (associated with the motion and position of the molecules, energy associated with the structure of the atom, chemical energy etc), which cannot be measured directly and is the summation of all microscopic energies is called internal energy of the system.

Internal energy:

It is the energy associated with internal structure of matter. This energy can not be determined in its absolute values. But it is possible to determine the change in internal energy of the system undergoing a process by first law of thermodynamics.

Total energy E = KE + PE + IE

$\therefore$

Since the terms comprising E are point functions, we can write

$dE = d(KE) + d(PE) + dU$

The first law of thermodynamics for a change of state of a system may therefore be written as

$\delta Q = dU + d(KE) + d(PE) + \delta W$

In words this equation states that as a system undergoes a change of state, energy may cross the boundary as either heat or work, and each may be positive or negative. The net change in the energy of the system will be exactly equal to the net energy that crosses the boundary of the system. The energy of the system may change in any of three ways, namely, by a change in IE, KE or P.E

Sub. For KE and PE in the above equation

$$Q = dU + \frac{d(mV^2)}{2} + d(mgZ) + W$$

In most of the situations the changes in KE and PE are very small, when compared with the changes in internal energies. Thus KE and PE changes can be neglected.

$\therefore \delta Q = dU\ \delta W$

Law of conservation of energy (2nd corollary of first law of thermodynamics)

From first law of thermodynamics $Q_{1-2} = E_2 - E_1 + W_{1-2}$

This equation in effect, a statement of the conservation of energy. The net change of the energy of the system is always equal to the net transfer of energy across the system boundary as heat and work. For an isolated system, $Q = 0$, $W = 0$ $E_2 - E_1 = 0$

For an isolated system, the energy of the system remains constant.

Therefore, the first law of thermodynamics may also be stated as follows, “Heat and work are mutually convertible but since energy can neither be created nor destroyed, the total energy associated with an energy conversion remains constant”.

Perpetual Machine of first kind (3rd Corollary):

Any system which violates the first law of thermodynamics is called the Perpetual Motion machine of first kind. i.e., “It is impossible to construct a perpetual motion machine of first kind”. A perpetual machine is one which can do continuous work without receiving energy from other systems or surroundings. It will create energy on its own and thus violates first law. But from our experience we also know that it is impossible to construct such a machine, as frictional resistance would not allow it to run for an indefinite period.

Problems:

1. In a cyclic process, heat temperature are + 14.7 kJ, -25.2 kJ, -3.56 kJ and +31.5 kJ. What is the net work for this cyclic process.

Solution: 1st law of thermodynamics for a cyclic process is

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

i.e., Net work = 14.7 – 25.2 -3.56 + 31.5= 17.44 kJ

2. Consider a cyclic process in a closed system which includes three heat interactions, namely $Q_1 = 20$ kJ, $Q_2 = -6$kJ, and $Q_3 = -4$ kJ and two work interactions for which $W_1 = 4500$ N-m. Compute the magnitude of the second work interaction W_2 in Nm.

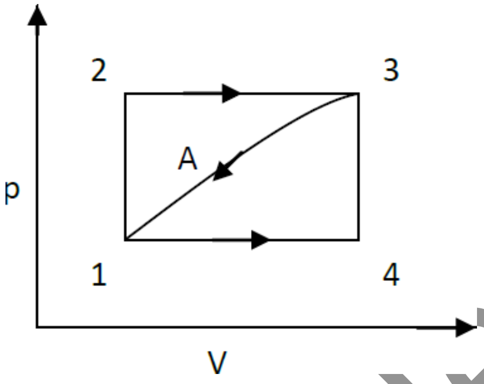
Solution: We have for a closed system undergoing cyclic process,

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

$$20000 - 6000 - 4000 = 4500 + W_2$$

$$W_2 = 5500 \text{ Nm}$$

3. When the state of a system changes from state 1 to state 3 along the path 1-2-3 as shown in figure, 80 kJ of heat flows into the system and the system does 30 kJ of work. (a) How much heat flows into the system along the path 1-4-3 if work done by the system is 10 kJ (b) when the state of the system is returned from state 3 to state 1 along the curved path, the work done on the system is 20 kJ. Does the system absorb or liberate heat? Find its magnitude. (c) If $U_1 = 0$ and $U_4 = 40$kJ, find the heat absorbed in the process 1-4 and 4-3 respectively. Solution:



a) Along the path 1-2-3,

From 1st law of thermodynamics, $Q_{1-3} = U_3 - U_1 + W_{1-3}$

From the data given, $80 = (U_3 - U_1) + 30$ $(U_3 - U_1) = 50$ kJ

Along the path 1-4-3, we have

$Q_{1-3} = U_3 - U_1 + W_{1-3}$

From the data given, $Q_{1-3} = 50 + 10$

= 60 Kj

i.e., Work is done by the system

b) Along the path 3-A-1,

$(U_1 - U_3) = Q_{3-1} - W_{3-1}$

Or $Q_{3-1} = (U_1 - U_3) + W_{3-1}$

= -50 -20 = -70 kJ

Negative sign indicates that heat is liberated from the system. c) Along the path 1-4

$Q_{1-4} = U_4 - U_1 + W_{1-4}$

= 40-0+10(since $W_{1-4-3} = W_{1-4} + W_{4-3} = 10 + 0 = 10$)

= 50 kJ

Positive sign indicates heat is absorbed by the system

Along the path 4-3

Q4-3 = U3 – U4 + W4-3

= 50 – 40 + 0 = 10 kJ

4. A domestic refrigerator is loaded with food and the door closed. During a certain period the machine consumes 1 kwhr of energy and the internal energy of the system drops by 5000 kJ. Find the net heat transfer. for the system.

Solution: W_{1-2} = 1 kWhr = -1 x3600 kJ $U_2 – U_1$ = -5000 kJ

From 1st law, $Q_{1-2} = (U_2-U_1) + W_{1-2}$

= -5000 -3600 = -8600 kJ = - 8.6 mJ

5. For the following process in a closed system find the missing data (all in kJ)

Process	Q	W	U1	U2	ΔU
a)	35	20	-10	5	15
b)	15	-6	-27	-6	21
c)	-7	10	20	3	-17
d)	-27	-7	28	8	-20

Solution: Process (a): Q = ΔU + W

$= U_2 – U_1 + W_{1-2}$ but $U_2-U_1 = 15$ $U_2 = 5$

= 15 + 20 = 35 kJ

Process (b): $Q = U_2 – U_1 + W$

$15 = -6-U_1-6$

$27 = -U_1$ $U_1 = -27$ kJ

$\Delta U = U_2 – U_1 = - 6 + 27 = 21$ kJ

Process (c) $- 7 = U_2 – 20 + 10$

$U_2 = 3$ kJ $\Delta U = 3-20 = -17$ kJ

Process (d) $\Delta U = U_2 – U_1 = - 20$

$= 8 – U_1 = - 20$ $U_1 = 28$ kJ

A = 8 – 28 – 7 = - 27 kJ

6. A fluid system, contained in a piston and cylinder machine, passes through a complete cycle of four processes. The sum of all heat transferred during a cycle is -340 kJ. The system completes 200 cycles minutes. Complete the following table showing the method for each item, and compute the net rate of work output in kW

Process	Q (kJ/min)	W (kJ/min)	ΔE (kJ/min)
1-2	0	4340	-4340
2-3	42000	0	42000
3-4	-4200	69000	-73200
4-1	-105800	-141340	35540

Solution: Given $\Sigma_{cycle} Q = -340$ kJ, No. of cycle = 200 cycles / min

Process 1-2: $Q_{1-2} = (E_2 - E_1) + W_{1-2}$

$0 = \Delta E + W_{1-2}$

$\therefore \Delta E = -4340$ kJ/min

Process 2-3: $42000 = \Delta E + 0$

$\therefore Q_{1-2} = 42000$ kJ/min

Process 3-4: $-4200 = -73200 + W_{3-4}$

$W_{3-4} = 69000$ kJ/min

Process 4-1: $\underset{cycle}{Q} = -340$ kJ

The system completes 200 cycle/min

$\therefore \underset{cycle}{\_\ Q} = -340 \text{ x } 200 = -68000$ kJ / min

But, $Q_{1-2} + Q_{2-3} + Q_{3-4} + Q_{4-1} = -68000$

$\therefore Q_{4-1} = -68000 - 0 - 42000 + 4200$

$= -105800$ kJ/min

Also, $\oint dE = 0$, since cyclic integral of any property is zero

$\therefore (\Delta E)_{1-2} + (\Delta E)_{2-3} + (\Delta E)_{3-4} + (\Delta E)_{4-1} = 0$

$-4340 + 42000 - 73200 + (\Delta E)_{4-1} = 0$

$\therefore (\Delta E)_{4-1} = 35540$ kJ/min

Therefore $Q_{4-1} = (\Delta E)_{4-1} + W_{4-1}$

$- 105800 = 35540 + W_{4-1}$

$\therefore W_{4-1} = -141340$ kJ/min

Since $\sum_{cycle} Q = \sum_{cycle} W$

$= - 68000$ kJ/min

Rate of work output $= \frac{68000}{60} = 1133.33$ kW

SECOND LAW OF THERMODYNAMICS

The first law states that when a closed system undergoes a cyclic process, the cyclic integral of the heat is equal to the cyclic integral of the work. It places no restrictions on the direction of the heat and the work. As no restrictions are imposed on the direction in which the process may proceed, the cycle may be reversed and it will not violate the first law.

Example (1):

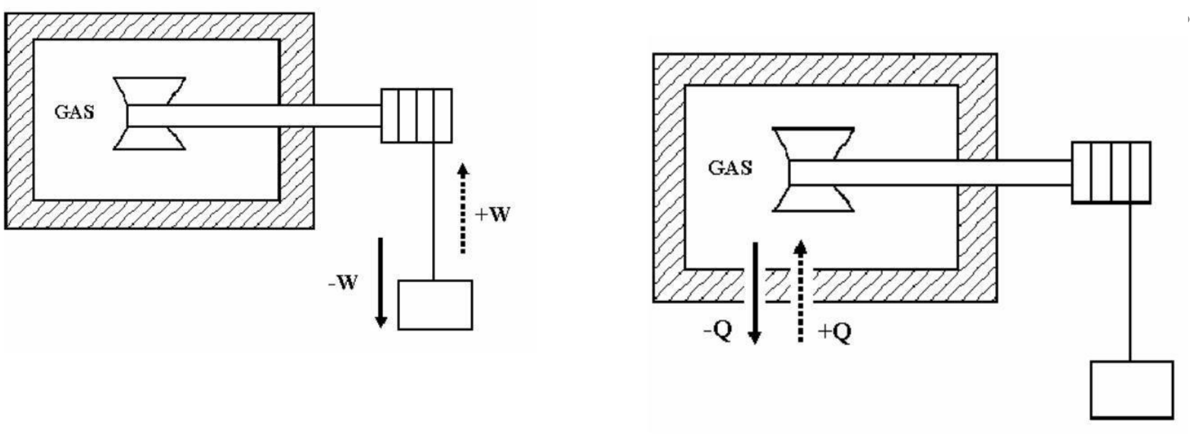
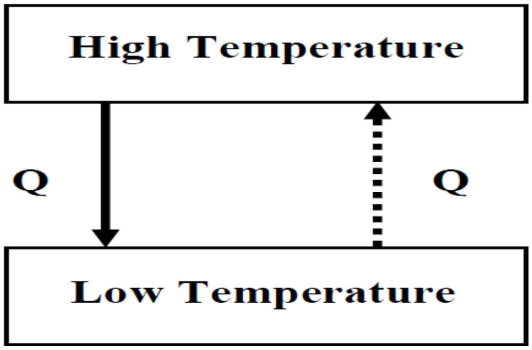


Fig: A closed system that undergoes a cycle involving work and heat.

In the example considered the system undergoes a cycle in which work is first done on the system by the paddle wheel as the weight is lowered. Then let the cycle be completed by transferring heat to the surrounding.

From experience it has been learnt that we cannot reverse this cycle. i.e., if we transfer heat to the gas, as shown by the dotted line, the temperature of the gas will increase, but the paddle wheel will not turn and lift the weigh. This system can operate in a cycle in which the heat and work transfers are both negative, but it cannot operate in a cycle when both are positive, even though this would not violate the first law

Example (2):



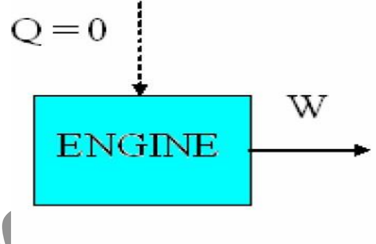
Let two systems, one at a high temperature and the other at a low temperature undergoes a process in which a quantity of heat is transferred from the high – temperature system to the low temperature system. From experience we know that this process can take place. But the reverse process in which heat is transferred from the low temperature system to the high temperature system does not occur and that it is impossible to complete the cycle by heat transfer only.

These two examples lead us to the consideration of the heat engine and heat pump (i.e., refrigerator).

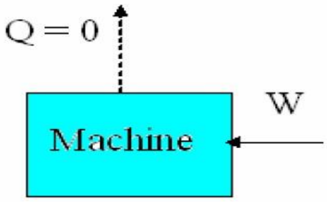
Experience tells us that the reversed processes described above do not happen. The total energy of each system would remain constant in the reversed process and thus there would be no violation of the first law. It follows that there must be some other natural principle in addition to the first law and not deducible from it, which governs the direction in which a process can take place in an isolated system. This principle is the Second law of thermodynamics.

PERPETUAL MOTION MACHINE OF FIRST KIND (PMMKI)

No machine can produce energy without corresponding expenditure of energy without corresponding expenditure of energy i.e., it is impossible to construct a PMMK of first kind. The machine violates the first law of thermodynamics. All attempts made so for to make PMMKI have failed, thus showing the validity of the first law.



A PMMK -I



The converse of A PMMK -I

Second law of Thermodynamics

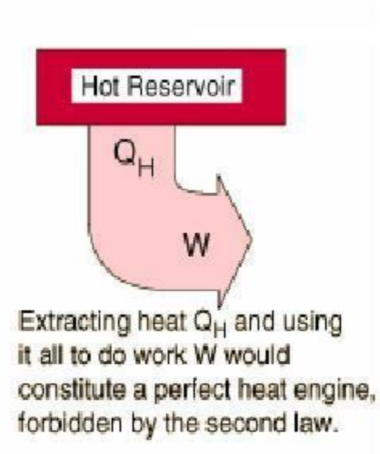
There are two classical statements of the second law of thermodynamics

1) Kelvin – Planck statement
2) Clausius statement

Kelvin – Planck statement

“It is impossible to construct a device which will operate in a cycle & produce no effect other than the raising of a weight and the exchange of heat with a single reservoir”

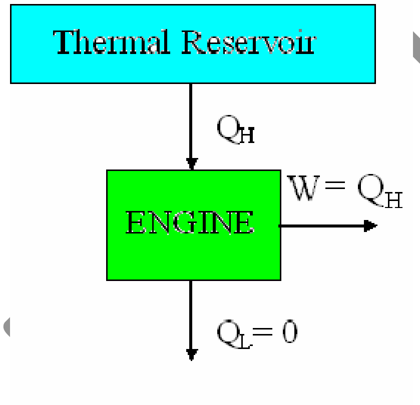
No actual or ideal engine operating in cycles can convert into work all the heat supplied to the working substance, it must discharge some heat into a naturally accessible sink because of this aspect and the second law is often referred as the law of degradation of energy.



Extracting heat Q_H and using it all to do work W would constitute a perfect heat engine, forbidden by the second law.

A directional implication of the 2nd Law

PERPETUAL MOTION MACHINE OF SECOND KIND (PMMKII)



A PMMK -II

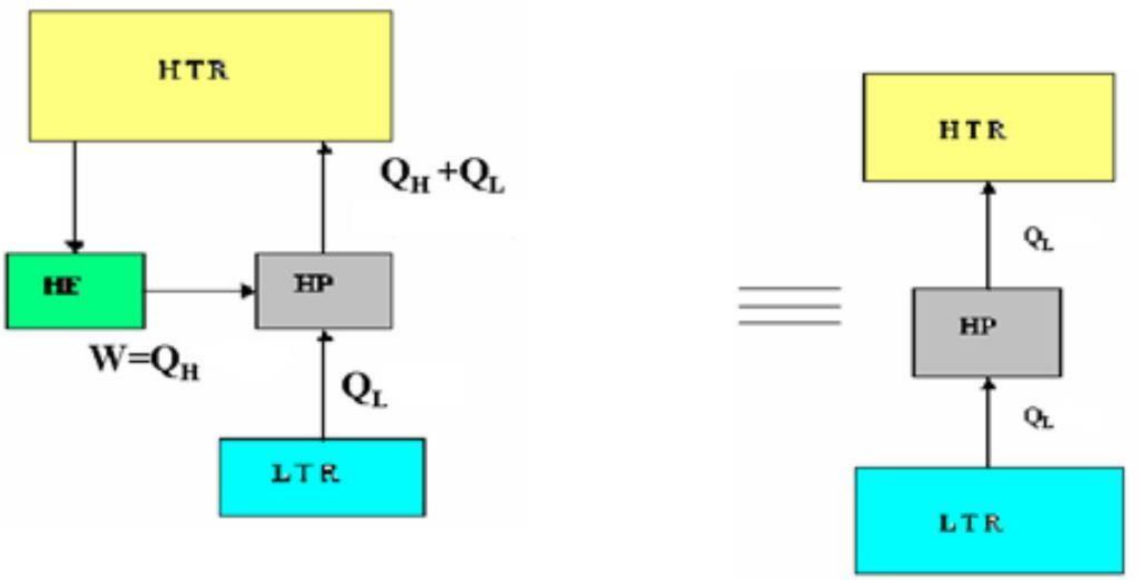
Without violating the first law a machine can be imagined which would continuously absorb heat from a single thermal reservoir and would convert this heat completely into work. The efficiency of such a machine would be 100%. This machine is called PMMK II. A machine of this kind will violate the second law of thermodynamics and hence does not exist.

Clausius Statement

It is impossible to construct a heat pump which operating in a cycle will produce no effect other than the transfer of heat from a low temperature thermal reservoir to a higher temperature thermal reservoir.

That is in order to transfer heat from a low temperature thermal reservoir to a high temperature thermal reservoir work must be done on the system by the surroundings. Although the Kelvin – Planck and Clausius statements appear to be different, they are really equivalent in the sense that a violation of one statement involves violation of the other.

Proof of violation of the Kelvin – Plank statement results in violation of the Clausius statement.

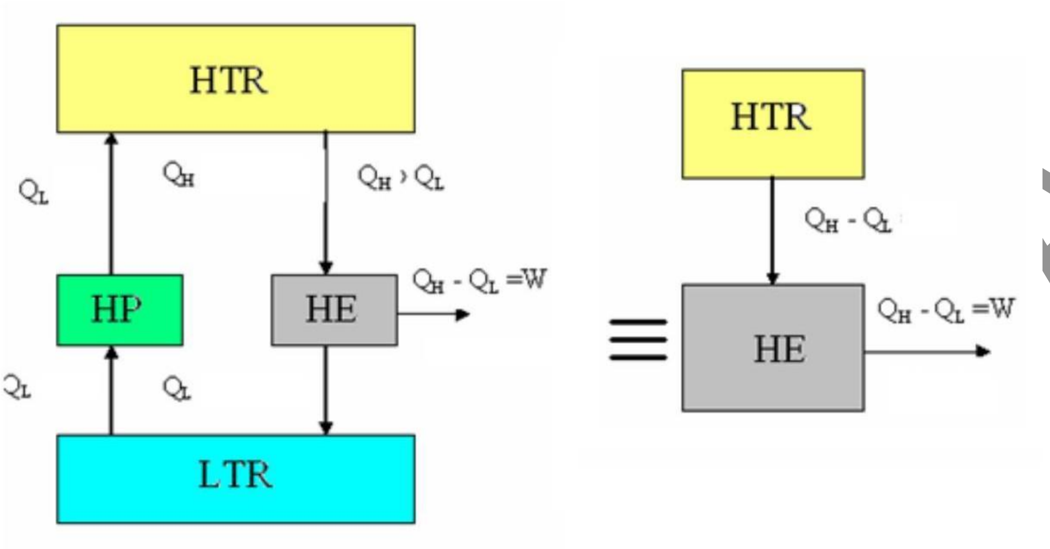


Consider a heat engine that is operating in a cyclic process takes heat (Q_H) from a high temperature reservoir & converts completely into work (W), violating the Kelvin – Planck statement.

Let the work W, which is equal to Q_H, be utilized to drive a heat pump as shown. Let the heat pump take in Q_L amount of heat from a low temperature reservoir and pump ($Q_H + Q_L$) amount of heat to the high temperature reservoir.

From the diagrams we see that a part of heat Q_H, pumped to the high temperature reservoir is delivered to the heat engine, while there remains a heat flow Q_L, from the low temperature reservoir to the high temperature reservoir, which in fact violates the clausius statement.

Proof of violation of the Clausius statement results in violation of the Kelvin – Planck statement.



Consider a heat pump that operating in a cyclic process takes in an amount of heat Q_L from LTR and transfer the heat equivalent amount of heat Q_L to the HTR violating the Clausius statement.

Let an amount of heat Q_H, which is greater than Q_L, be transferred from high temperature reservoir to a heat engine, an amount of heat Q_L, be rejected by it to the LTR and an amount of work W which is equal to ($Q_H – Q_L$) be done by the heat engine on the surrounding.

Since there is no change in heat transfer in the LTR, the heat pump, the HTR and the heat engine together can be considered as a device which absorbs an amount of heat ($Q_H – Q_L$) from the HTR and produce an equal amount of work W = $Q_H - Q_L$ which in fact violates the Kelvin – Planks statement.

Reversibility and Irreversibility

If 100% efficiency is unattainable, what is the max possible efficiency which can be attained and what factors promote the attainment of this max value? In trying to answer these questions, thermodynamics has invented & used the concept of reversibility, absolute temperature and entropy.

Reversible Process:

For a system is defined as a process which once having taken place, can be reversed and leaves no change in either the system or surroundings. Only ideal processes can do this and restore both system and surroundings to their initial states. Hence an ideal process must be a reversible process.

No real process is truly reversible but some processes may approach reversibility, to a close approximation.

Example:

1) Frictionless relative motion
2) Extension and compression of a spring
3) Frictionless adiabatic expansion or compression of fluid.
4) Polytropic expansion or compression etc.,

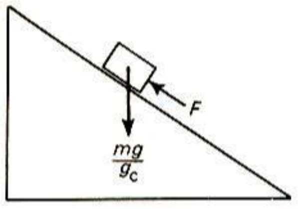
The conditions for a process to be reversible may be given as follows:

1. There should be no friction
2. There should be no heat transfer across finite temperature difference.
3. Both the system and surrounding be stored to original state after the process is reversed.

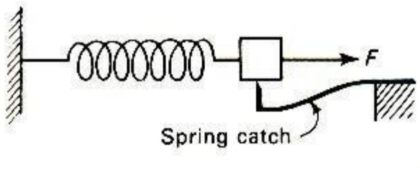
   Any process which is not reversible is irreversible.

Example: Movement of solids with friction, A flow of viscous fluid in pipes and passages mixing of two different substances, A combustion process, every quasi-static process is reversible, because a quasi-static process is of an infinite succession of equilibrium states.

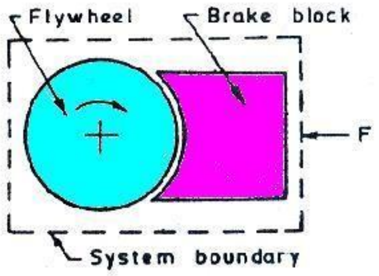
Examples of Irreversible processes:



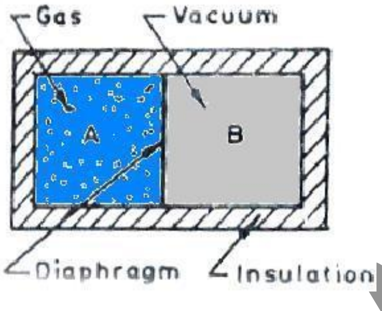
(a) Frictionless relative motion



(b) Extension of a spring

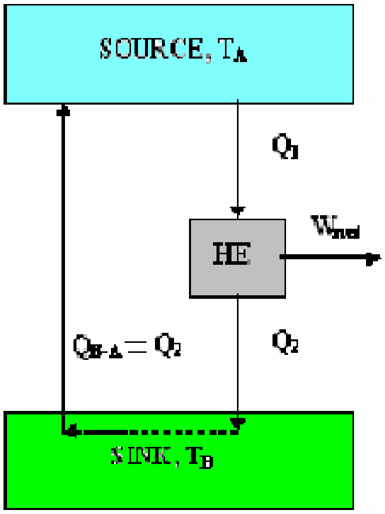


(i) Solid Friction

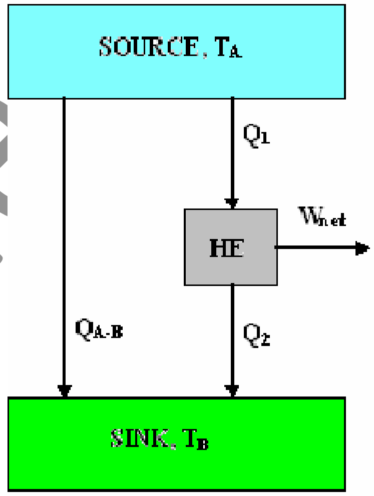


(ii) Free expansion

Proof that heat transfer through a finite temperature difference is irreversible

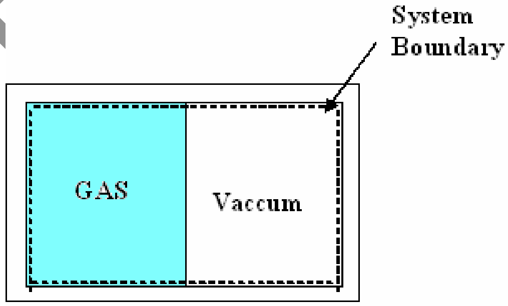


Heat transfer through a finite temperature difference

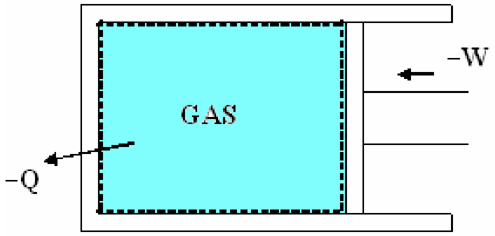


Heat transfer through a finite temperature difference is irreversible

Proof that unrestrained expansion makes process irreversible



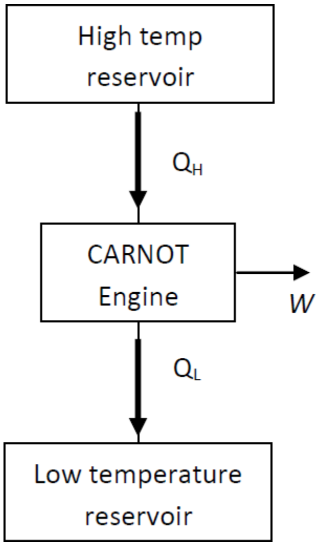
INTIAL STATE



REVERSED PROCESS

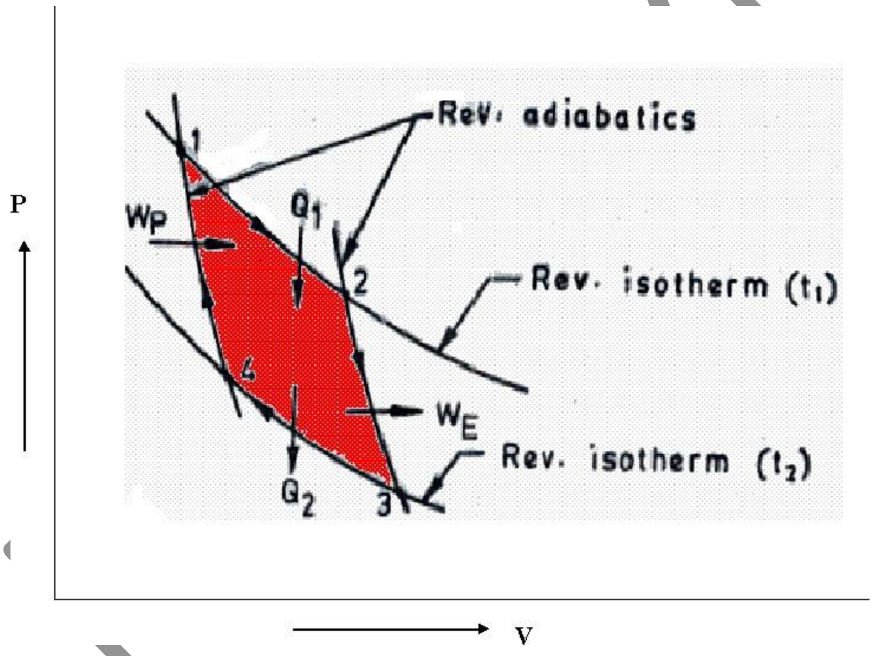
THE CARNOT CYCLE:

Carnot was the first man to introduce the concept of reversible cycle. The CARNOT engine works between HTR & LTR.



The Carnot cycle consists of an alternate series of two reversible isothermal and two reversible adiabatic processes. Since the processes in the cycle are all reversible the Carnot cycle as a whole is reversible.

The Carnot cycle is independent of the nature of the working substance and it can work with any substance like gas, vapour, electriccell.



CARNOT CYCLE

1) Process 1–2: Gas expands isothermally absorbing heat Q_1 from the source at Temperature T_1. Work done during this process is given by the area under 1 – 2 (W_{12})

2) Process 2–3: During this process cylinder is thermally isolated from the heat reservoir and the head is insulated by the piece of perfect insulator. Gas expands reversibly and adiabatically to temperature T_2 to point 3. Work done is W_{23}.

3) Process 3–4: Cylinder is in contact with the heat reservoir at T_2. Gas is isothermally and reversibly compressed to point 4 rejecting an amount of heat Q_2 to the sink. The work done on the W_{34}.

4) Process 4–1: Cylinder is again isolated thermally from the thermal reservoir; gas is recompressed adiabatically and reversibly to point 1. The cycle is now complete. Work done is W_{41}

The efficiency of the Carnot engine is given by,

$$\eta_{carnot} \quad \frac{Work\ output}{Heat\ input} \quad \frac{Q_1 - Q_2}{Q_1} \qquad (1)$$

$$Q_1 \quad \text{Heat added during process 1} \;\text{-}2 \quad mRT_1 \ln \frac{V_2}{V_1} \qquad (2)$$

$$Q_2 \quad \text{Heat } \textit{rejected} \text{ during process } 3 \quad 4 \; mRT_2 \ln \frac{V_3}{V_4} \qquad (3)$$

Therefore, $$\eta_{carnot} \quad \frac{Q_1 - Q_2}{Q_1} \quad \frac{mRT_1 \ln \frac{V_2}{V_1} \quad mRT_2 \ln \frac{V_3}{V_4}}{mRT_1 \ln \frac{V_2}{V_1}} \qquad (4)$$

Since process 2 – 3 is reversible adiabatic

$$\frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} ----------- (5)$$

Process 4 – 1 is also reversible adiabatic

$$\frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}, \text{Therefore}, \frac{V_2}{V_3} = \frac{V_1}{V_4} \text{ or } \frac{V_2}{V_1} = \frac{V_3}{V_4} ----------- (6)$$

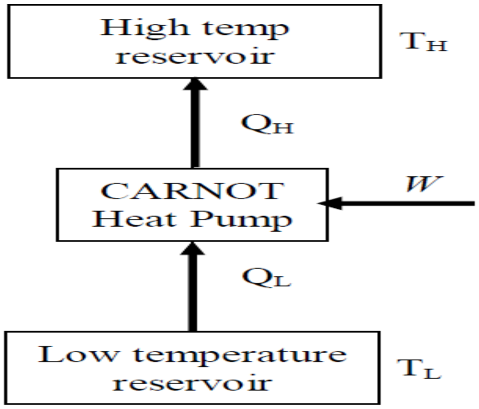
$$\eta_{carnot} = \frac{T_1 - T_2}{T_1} ----------- (7)$$

$$\eta_{carnot} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} = 1 - \frac{\text{Low Temperature}}{\text{High Temperature}} ---------- (8)$$

From the above equation we can have the following conclusions.

Even in an ideal cycle, it is impossible to convert all the energy received as heat from the source into mechanical work. We have to reject some of the energy as heat to a receiver at a lower temperature than the source (sink).

Since Carnot cycle consists of reversible processes, it may be performed in either direction.



Carnot heat pump with a gas

Process 1 - 4	Reversible adiabatic expansion	Temperature falls down from T_H to T_L
Process 4 - 3	Reversible isothermal expansion	Temperature remains constant
Process 3 - 2	Reversible adiabatic Compression	Temperature increases from T_L to T_H
Process 2 - 1	Reversible isothermal Compression	Temperature remains constant

$$\text{COP}_{\text{ of heat pump}} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L}$$

$$\text{COP}_{\text{ of refrigerator}} = \frac{Q_L}{W} \quad \frac{Q_L}{Q_H \quad Q_L} \quad \frac{T_L}{T_H \quad T_L}$$

Problems:

A heat engine works on the Carnot cycle between temperature 900° C & 200° C. If the engine receives heat at the higher temperature at the rate of 60 kW, calculate the power of the engine.

$T_H = 900 + 273 = 1173$ k

$T_L = 200 + 273 = 473$ k

$$\eta = \frac{T_H - T_L}{T_H} = \frac{1173 - 473}{1173} = 0.597$$

Also, $$\eta_{th} = \frac{W}{Q_H} = \frac{\dot{W}}{\dot{Q}_H} \Rightarrow \dot{W} = \eta_{th} \dot{Q}_H$$

$$\therefore \dot{W} = 0.597 \text{ x } 60 = 35.82 \text{ kW}$$

Carnot theorem and corollary "An irreversible heat engine can not have an efficiency greater than a reversible one operating between the given two temperatures".

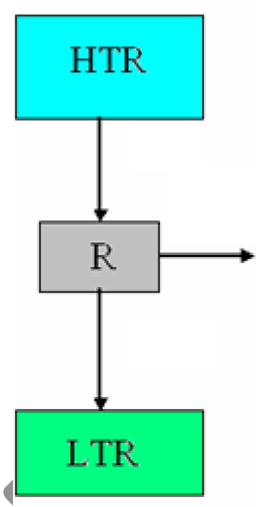


Fig. (a)

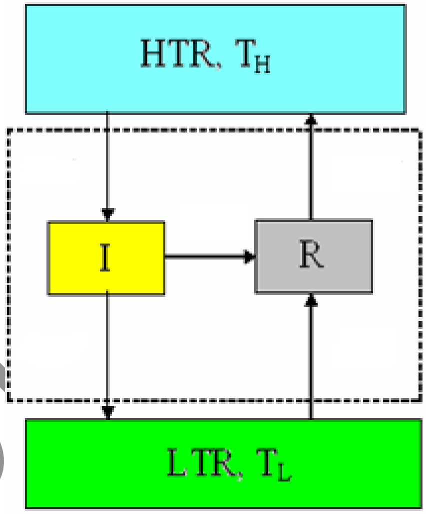


Fig. (b)

In other words, for the assumed condition that I is more efficient than R, we find that heat is being moved continuously from LTR to HTR without the external aid.

Instead of simply moving the heat as shown in fig (b), we could direct the flow of energy from the reversible engine directly into the irreversible engine, as in fig (c), whose efficiency is 50%

would allow to drive engine R, and at the same time deliver 10 KJ of work to something outside of the system. This means the system exchanges heat with a single reservoir and delivers work.

These events have never been known to happen.

We say that the assumption that I is more efficient than R is impossible

$$\therefore \eta_I \leq \eta_R$$

Corollary

All reversible engines have the same efficiency when working between the same two temperatures.

Consider two reversible engines $\mathbf{R_1}$ and $\mathbf{R_2}$, operating between the two temperatures. If we imagine R_1 driving R_2 backward, then Carnot theorem states that.

If R_2 drives R_1 backward, then

$$\eta_{R_2} < \eta_{R_1}$$

It therefore follows that

$$\eta_{R_1} = \eta_{R_2}$$

If this were not so, the more efficient engine could be used to run the less efficient engine in the reverse direction and the net result would the transfer of heat from a body at low temperature to a high temperature body. This is impossible according to the second law.

Suppose $\mathbf{R_1}$ & $\mathbf{R_2}$ are two reversible engines working between the two same reservoirs as shown let us assume that $\mathbf{R_1}$ is more efficient than $\mathbf{R_2}$. By our assumption

The Thermodynamics Temperature Scale

Zeroth law provides a basis for temperature measurement, but it has some short comings, since the measurement of temperature depends on the thermometric property of a particulars substance and on the mode of working of the thermometer.

With this principle lord Kelvin device a temperature scale that is independent of the thermometric property of the working substance and this is the Kelvin temperature scale or thermodynamic temperature scale or absolute temperature scale.

Problems (on second Law of thermodynamics)

Problem 1. An engineer claims to have developed an engine which develops 3.4 kW while consuming 0.44 Kg of fuel of calorific value of calorific value of 41870 kJ / kg in one hour. The maximum and minimum temperatures recorded in the cycle are 1400° C & 350° C respectively is the claim of the engineer genuine (Sept./Oct. 1996)

Solution:

Temperature of source, T_H = 1400° C = 1673 K

Temperature of sink, T_L = 350° C = 673 K

We know that the thermal efficiency of the CARNOT cycle is the maximum between the specified temperature limits and is given as.

$$\eta_{carnot} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

$$\text{i.e., } \eta_{carnot} = 1 - \frac{T_L}{T_H} = 1 - \frac{623}{1673} = 0.628$$

$$= 62.8\%$$

The thermal efficiency of the engine developed by the engineer is given as

$$\eta_{thermal} = 1 - \frac{\dot{Q}_L}{\dot{Q}_H} = \frac{\dot{W}}{\dot{Q}_H}$$

We have, $\dot{W} = 3.4\ kW$

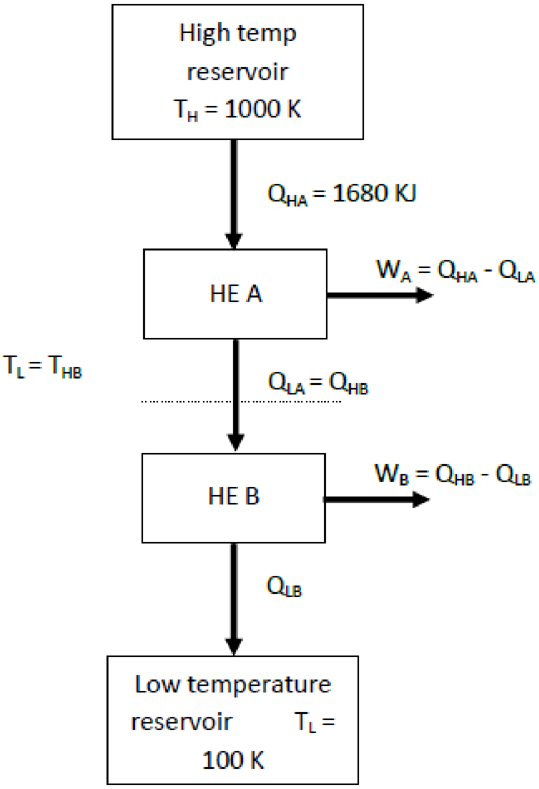
$$\dot{Q}_H = \frac{0.44\ x\ 41870}{3600} = 5.12\ kW$$

$$\&\ \eta_{thermal} = \frac{3.4}{5.12} = 0.664\ or\ 66.4\%$$

Since $\eta_{thermal} > \eta_{Carnot},$ Engineer claim is not genuine **Answer**

Problem 2. Two Carnot engines A and B are connected in series between two thermal reservoirs maintained at 100 k and 100 k respectively. Engine A receives 1680 kJ of heat from the high temperature reservoir and rejects heat to Carnot engine B. Engine B takes in the heat rejected by engine A and rejects heat to the low temperature reservoir. If engines A and B have equal thermal efficiencies determine (1) The heat rejected by engine B (2) The temperature at which heat is rejected by engine A and (3) The work done during the process by engines A and B respectively.

Solution:



Q_{HA} = 1680 KJ

$$\eta_A = \eta_B$$

We have,

$$\eta_A = 1 - \frac{Q_{LA}}{Q_{HA}}$$

$$= 1 - \frac{T_{LA}}{T_H}$$

$$\& \ \eta_B = 1 - \frac{Q_{LB}}{Q_{HB}}$$

$$= 1 - \frac{T_L}{T_{HB}}$$

i) Given $\eta_A = \eta_B$

$$\therefore 1 - \frac{T_{LA}}{T_H} = 1 - \frac{T_L}{T_{HB}}$$

$$i.e, \quad \frac{T_L}{T_{HB}} = \frac{T_{LA}}{T_H} \Rightarrow \frac{T_L}{T_{LA}} = \frac{T_{LA}}{T_H}$$

$$\text{i.e., } T^2{}_{LA} = T_L \times T_H = 100 \times 1000$$

$$= 100000 \text{ K}^2$$

[∴ $T_{LA} = T_{HB}$ = 316.23 K, i.e., the temperature at which heat is rejected by engine A]

ii) We have also

$$\eta_A = \eta_B = 1 - \frac{T_{LA}}{T_H} = 1 - \frac{316.23}{1000}$$

$$= 0.684 \text{ or } 68.4\%$$

The heat rejected by engine B

$$\eta_B = 1 - \frac{Q_{LA}}{Q_{HB}} = 1 - \frac{T_{LH}}{T_{HB}} = 1 - \frac{T_L}{T_{LA}}$$

$$i.e, \frac{Q_{LB}}{Q_{HB}} = \frac{T_L}{T_{LA}} \Rightarrow Q_{LB} = Q_{HB}\frac{T_L}{T_{LA}} \text{---------(1)}$$

We have,

$$\eta_A = 1 - \frac{Q_{LA}}{Q_{HA}} = 1 - \frac{T_{LA}}{T_H}$$

$$\text{i.e., } Q_{LA} = Q_{HA}\frac{T_{LA}}{T_H} = 1680 \times \frac{316.23}{1000}$$

$$= 531.27 \text{ KJ} = Q_{HB}$$

Substituting this in (1) we get

$$Q_{LB} = 531.27 \times \frac{100}{316.23} = 168KJ \quad \text{Ans.}$$

iii) Work done

$$W_A = Q_{HA} - Q_{LA} = 1680 - 531.27 = 1148.73 \text{KJ}$$

$$W_B = Q_{HB} - Q_{LB} = 531.27 - 168 = 363.27 \text{KJ}$$

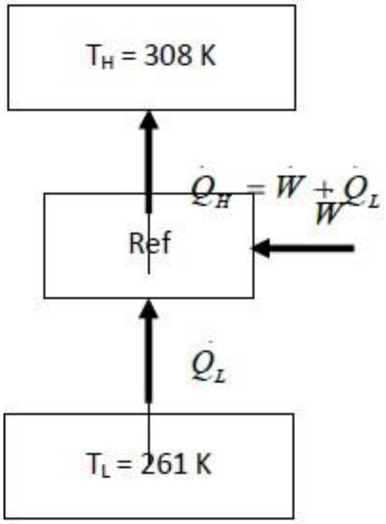
Problem 3. A reversible refrigerator operates between 35° C and -12° C. If the heat rejected to 35° C reservoir is 1.3 kW, determine the rate at which to heat is leaking into the refrigerator.

Solutions: Reversible refrigerator

$$T_H = 35^\circ\ C = 308\ K$$

$$T_L = -12^\circ\ C = 261\ K$$

$$(COP)\ Ref = \frac{\dot{Q}_L}{\dot{W}} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L}$$



$$= \frac{T_L}{T_H - T_L} \quad (\because \text{It is a reversible refrigerator})$$

$$\text{i.e,}\ \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} = \frac{T_L}{T_H - T_L} = \frac{261}{308 - 261}$$

$$= 5.553$$

$$\text{i.e,}\ \dot{Q}_L = 5.553\left[\dot{Q}_H - \dot{Q}_L\right] = 5.553\,\dot{Q}_H - 5.553\,\dot{Q}_L$$

$$\text{i.e.,}\ \dot{Q}_L + 5.553\,\dot{Q}_L = 5.553\,\dot{Q}_H$$

$$\text{i.e.,}\ \dot{Q}_L = \frac{5.553}{6.553} \times \dot{Q}_H = \frac{5.553}{6.553} \times 1.3 \qquad = 1.102\ \text{kW}\quad \text{Ans.}$$

MODULE-3

ENTROPY

The first law of thermodynamics introduces the concept of the internal energy U, and this term helps us to understand the nature of energy, as defined by the first law. In the similar way the second law introduces the concept of entropy S, like internal energy it is also a thermodynamic property and is defined only in terms of mathematical operations.

CLAUSIUS THEOREM:

The thermal efficiency of reversible Carnot cycle is given by the expression

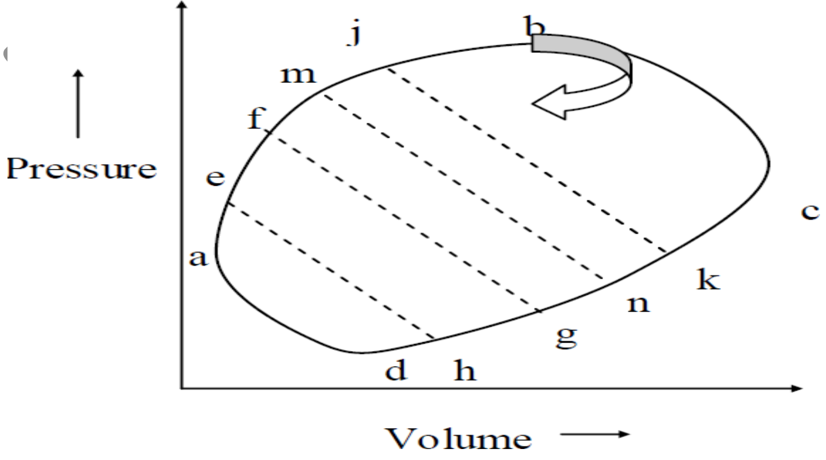
$$\eta_{Carnot} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \; or \; \frac{Q_H}{T_H} = \frac{Q_L}{T_L} \quad --------- (1)$$

Where T_H and T_L are the temperatures of high temperature thermal reservoir and low temperature thermal reservoir respectively, and Q_H is the heat supplied and Q_L is the heat rejected by the Carnot engine.

Considering the usual sign convention, +ve for the heat absorbed and –ve for the heat rejected, we may write,

$$\frac{Q_H}{T_H} = -\frac{Q_L}{T_L} \; or \; \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \quad ---------- (2)$$

The above conclusion is for the Carnot reversible cycle. But it can be proved that the conclusion is valid for any reversible cycle. Consider any arbitrary reversible cycle a-b-c-d-a as shown. In such cycle absorption and rejection of heat do not occur at two constant temperatures but take place at continuously changing temperatures.



The cycle can be now broken into an infinite number elementary Carnot cycle by drawing a series of infinitely close adiabatic lines, eh, fg, mn, etc. efgh, fmng etc represents elementary Carnot cycle in which sections ef, gh etc can be considered as isothermal lines.

For any differential Carnot cycle, efgh, let Q_{H1} be the heat absorbed during isothermal process ef and Q_{L1} be the heat rejected during the isothermal process gh. The temperature of ef is T_{H1} and gh process is T_{L1}.Then we may write,

$$\frac{Q_{H1}}{T_{H1}} = \frac{Q_{L1}}{T_{L1}}$$

Using proper sign convention +ve for the absorption of heat and -ve for rejection, we get,

$$\frac{Q_{H1}}{T_{H1}} + \frac{Q_{L1}}{T_{L1}} = 0 ---------(1)$$

Similarly,

$$\frac{Q_{H2}}{T_{H2}} + \frac{Q_{L2}}{T_{L2}} = 0 ---------(2)$$ for the cycle fmng

From these relations we see that the algebraic sum of the ratios of the amounts of heat transferred to the absolute temperature for the Carnot cycles taken together is equal to zero, thus,

$$\left(\frac{Q_{H1}}{T_{H1}} + \frac{Q_{L1}}{T_{L1}}\right) + \left(\frac{Q_{H2}}{T_{H2}} + \frac{Q_{L2}}{T_{L2}}\right) + ---------- = 0$$

$$\text{i.e. } \sum\left(\frac{Q_H}{T_H} + \frac{Q_L}{T_L}\right) = 0 ----------(3)$$

As the number of Carnot cycles is very large, the sum of the terms $\frac{Q}{T}$ over the complete cycle becomes equal to the cyclic integral of $\frac{Q}{T}$, We may , therefore write

$$\oint_R \frac{\delta Q}{T} = 0 ---------(4)$$

Where R represents reversible cycle. This result is known as **CLAUSIUS THEOREM.** $\frac{\delta Q}{T}$ is

ENTROPY:

Definition: Entropy , S is a property of system such that its increase **S_2 - S_1** as the system changes from state 1 to state 2 is given by,

$$S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T} \quad -----------(1)$$

In differential form equation (1) can be written as $dS = \frac{\delta Q_R}{T}$

THE CLAUSIUS INEQUALITY:

When any system undergoes a cyclic process, the integral around the cycle of $\frac{\delta Q}{T}$ is less than or equal to zero.

In symbols, $\oint \frac{\delta Q}{T} \leq 0 -------(1)$

Where **δQ is** an infinitesimal heat transfer**, T is** absolute temperature of the part of the system to which heat transfer **δQ** occurs**.**

PROOF: For any reversible cycle from Clausius theorem,

$$\oint_R \frac{\delta Q}{T} = 0 ---------(2)$$

From the Carnot's theorem we know that the efficiency of an irreversible engine is less than that of a reversible engine, i.e. $\eta_I \langle \eta_R$

Where η_I is efficiency of the irreversible engine and η_R is efficiency of the reversible engine

Hence, $1 - \left(\frac{\delta Q_L}{\delta Q_H}\right)_I \langle 1 - \left(\frac{\delta Q_L}{\delta Q_H}\right)_R ------------(3)$

Where I and R represents irreversible and reversible processes respectively.

For a reversible engine, the ratio of the heat absorbed and heat rejected is equal to the ratio of the absolute temperatures. Therefore

$$1-\left(\frac{\delta Q_L}{\delta Q_H}\right)_I \langle\ 1-\left(\frac{T_L}{T_H}\right)------------(4) \qquad \text{i.e.} \left(\frac{\delta Q_L}{\delta Q_H}\right)_I \rangle \left(\frac{T_L}{T_H}\right)$$

$$\text{or} \left(\frac{\delta Q_H}{\delta Q_L}\right)_I \langle \left(\frac{T_H}{T_L}\right) \quad \textbf{i.e.} \left(\frac{\delta Q_H}{T_H}\right)_I - \left(\frac{\delta Q_L}{T_L}\right)_I \langle\ 0\ -------(5)$$

Using sign conventions of +ve for absorption of heat and –ve for the rejection of heat , we get,

$$\left(\frac{\delta Q_H}{T_H}\right)_I + \left(\frac{\delta Q_L}{T_L}\right)_I \langle\ 0\ -------(6)$$

From this we see that the algebraic sum of the ratios of the amounts of heat transferred to the absolute temperature for a cyclic irreversible process is always less than zero,

$$\oint_I \frac{\delta Q}{T} \langle\ 0---------(7)$$

Combining equations (2) and (7), we get $\oint \frac{\delta Q}{T} \leq 0---------(8)$

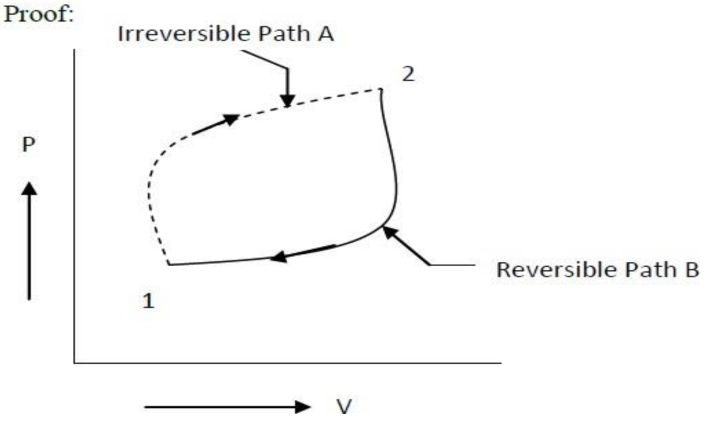
This is known as **CLAUSIUS INEQUALITY**.

CALCULATION OF ENTROPY CHANGE FOR DIFFERENT PROCESS

Entropy change in **IRREVERSIBLE** process:

For a process that occurs irreversibly, the change in entropy is greater than the heat change divided by the absolute temperature. In symbols, $dS \rangle \frac{\delta Q}{T}$

Proof:



Consider an arbitrary irreversible cycle 1-A-2-B-1 as shown in figure. The path 1 to 2(1-A-2) is traversed irreversibly and the path 2 to 1 (2-B-1) reversibly. From the Clausius Inequality, we have

$\oint \frac{\delta Q}{T} \langle\ 0$, for the cycle which is irreversible and

$\oint \frac{\delta Q}{T} = 0$, for the cycle which is reversible ---------------------------- (1)

Since the entropy is a thermodynamic property, we can write

$$\oint dS = \int_{1A}^{2} dS_I + \int_{2B}^{1} dS_R = 0 \quad -----(2)$$

For a reversible process we have, $\int_{2B}^{1} dS_R = \int_{2B}^{1} \frac{\delta Q_R}{T} \quad -----(3)$

Substituting this in equation (2), we get

$$\int_{1A}^{2} dS_I + \int_{2B}^{1} \frac{\delta Q_R}{T} = 0 \quad -----(4)$$

Using equation (1), for an irreversible cycle,

$$\oint \frac{\delta Q}{T} = \int_{1A}^{2} \left(\frac{\delta Q}{T}\right)_I + \int_{2B}^{1} \left(\frac{\delta Q}{T}\right)_R \ \langle\ 0 \quad -----(5)$$

Now subtracting equation (5) from equation (4), we get

$$\int_{1A}^{2} dS_I \ \rangle \ \int_{1A}^{2} \left(\frac{\delta Q}{T}\right)_I \qquad -----(6)$$

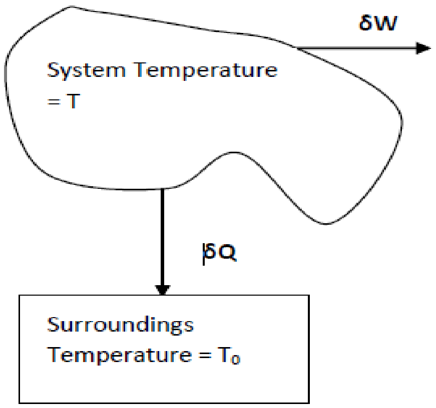
For small changes in states the above expression can be written as,

$$dS_I \ \rangle \left(\frac{\delta Q}{T}\right)_I \qquad -----(7)$$

PRINCIPLE OF THE INCREASE OF ENTROPY:

Entropy Change for the System + Surroundings

Consider the process shown. Let δQ is the heat transfer from a system at temperature **T** to the surroundings at temperature **T0, and δW** is the work of this process (either +ve or –ve). Using the principle of increase in entropy.



$$dS_{system} \ge -\frac{\delta Q}{T} ------(1)$$

$$dS_{surroundings} = \frac{\delta Q}{T_0} ------(2)$$

for a reversible process

The total change of entropy for the combined system

$$dS_{system} + dS_{surroundings} \ge -\frac{\delta Q}{T} + \frac{\delta Q}{T_0}$$

$$or\ dS_{system} + dS_{surroundings} \ge \delta Q\left(-\frac{1}{T} + \frac{1}{T_0}\right)$$

The same conclusion can be had for an open system, because the change in the entropy of the system would be

$$dS_{open\ system} \ge -\frac{\delta Q}{T} + \delta m_i s_i - \delta m_e s_e$$

The change in the entropy of the surroundings would be,

$$dS_{surroundings} = \frac{\delta Q}{T_0} - \delta m_i s_i + \delta m_e s_e$$

$$dS_{system} + dS_{surroundings} \ge -\frac{\delta Q}{T} + \frac{\delta Q}{T_0}$$

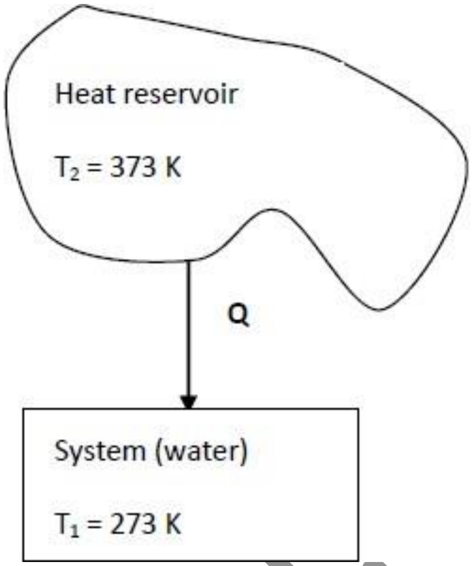
Therefore, $or\ dS_{system} + dS_{surroundings} \ge \delta Q\left(-\frac{1}{T} + \frac{1}{T_0}\right)$ since $T \rangle T_0$ and it follows

that $-\frac{1}{T} + \frac{1}{T_0} \rangle 0$ and therefore $dS_{system} + dS_{surroundigs} \ge 0$

Problems on entropy:

Problem No.1. One kg of water at 273 K is brought into contact with a heat reservoir at 373 K. When the water has reached 373 K, find the entropy change of water, the heat reservoir and of the universe.

Solution: Let T_1 be the temperature of water, T_2 be the temperature of heat reservoir. Since reservoir is at higher temperature than that of water, when water is brought into contact with the reservoir heat transfer occurs from reservoir to water and takes place through a finite temperature difference (irreversible). The entropy of water would increase and that of reservoir decrease so that net entropy change of the water and the reservoir together would be **+ve definite.** To find the entropy change of water we have to assume a reversible path between end states, which are at equilibrium.



1) Entropy of water

$$\Delta S_{water} = \int_{T_1}^{T_2} m c_p \frac{dT}{T} = m c_p \ln\frac{T_2}{T_1}$$

$$= 1 x 4.187 \ln\frac{373}{} = 1.3068 kJ/K$$

Problem No.2. Two kg of air is heated from 27^0C to 427^0C while the pressure changes from 100 kPa to 600 kPa. Calculate the change of entropy. $R = 0.257$ kJ / kg K, $C_p = 1.005$ kJ / kg K.

Solution: Given:

m = 2 kg	
$T_1 = 27 + 273 = 300K$ $T_2 = 427 + 273 = 700K$	$P_1 = 100$ kPa $P_2 = 600$ kPa

The general equation used for the calculation of change of entropy is given by,

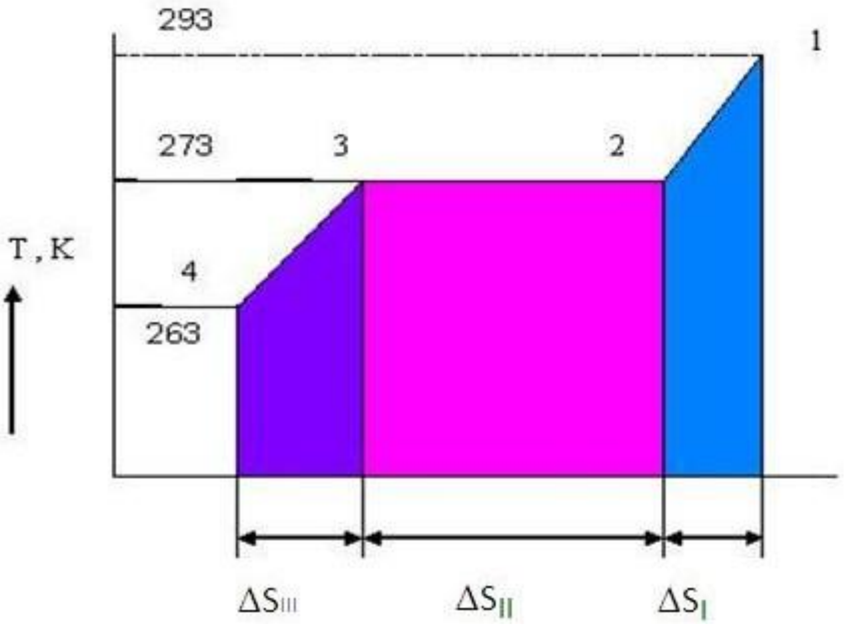
$$\Delta S_{air} = S_2 - S_1 = m\,c_p \ln\frac{T_2}{T_1} - m\,R\ln\frac{P_2}{P_1} = 2\,x\,1.005\ln\left[\frac{700}{300}\right] - 2\,x\,0.257\ln\left[\frac{600}{100}\right]$$

$$= 0.7821 kJ/K$$

Problem No.3. Ten grams of water at 20 ^{0}C is converted into ice at - 10 ^{0}C at constant atmospheric pressure. Assuming specific heat of liquid water to remain constant at 4.184 J / g ^{0}C and that of ice to be half of this value, and taking the latent heat of fusion of ice at 0 ^{0}C to be 335 J / g, calculate the total entropy change of the system.

Solution: Given :

m = 10 gm	
Water is available at temperature $T_1 = 20\ ^0C = 293$ k $C_{p(water)} = 4.184$ J / g ^{0}C = 4.184 kJ / kg ^{0}C	Ice is to be formed at temperature $T_4 = -10\ ^0C = 263$ K $C_{p(ice)} =$ ½ x 4.184 J / g ^{0}C = ½ x 4.184 kJ / kg ^{0}C



$$\Delta S_I = \int_{293}^{273} mc_p \frac{dT}{T} = mc_p \ln\frac{273}{293} = \frac{10}{1000} x\, 4.184 \ln\frac{273}{293}$$
$$= -2.958x10^{-3}\, kJ/K$$

b) ΔS_{II} i.e. entropy change of water at 0 ^{0}C.to become ice at 0 ^{0}C

$$\Delta S_{II} = -\frac{mQ_L}{T} = -\frac{10}{1000} x \frac{335}{273} = -0.0123 kJ/K$$

c) ΔS_{III} i.e. entropy change of ice as it is cooled from 0 ^{0}C to -10 ^{0}C

$$\Delta S_{III} = \int_{273}^{263} mc_{p(ice)} \frac{dT}{T} = mc_{p(ice)} \ln\frac{263}{273} = \frac{10}{1000} x \frac{4.184}{2} \ln\frac{263}{273}$$
$$= -7.807x10^{-4}\, kJ/K$$

Therefore total entropy change of water as it is converted into ice will be

$$\Delta S_{Total} = \Delta S_I + \Delta S_{II} + \Delta S_{III} = -2.958x10^{-3} + (-0.0123) + (-7.807x10^{-4})$$
$$= -0.01604 kJ/K$$

THE PURE SUBSTANCE

The system encountered in thermodynamics is often quite less complex and consists of fluids that do not change chemically, or exhibit significant electrical, magnetic or capillary effects. These relatively simple systems are given the generic name the Pure Substance.

Definition

A system is set to be a pure substance if it is (i) homogeneous in chemical composition, (ii) homogeneous in chemical aggregation and (iii) invariable in chemical aggregation.

Homogeneous in chemical composition means that the composition of each part of the system is same as the composition of any other part. Homogeneous in chemical aggregation implies that the chemical elements must be chemically combined in the same way in all parts of the system. Invariable in chemical aggregation means that the chemical aggregation should not vary with respect to time.

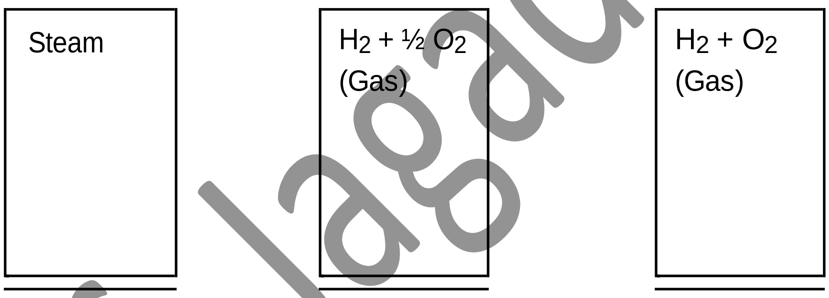


Figure: Illustration of the definition of pure substance

i)Satisfies condition ii) Does not satisfies condition (iii) are not pure substances

In figure three systems are shown. The system (i) shown in the figure is a mixture of steam and water. It is homogeneous in chemical composition because in every part of the system we have, for every atom of oxygen we have two atoms of hydrogen, whether the sample is taken from steam or water. The same is through for system (ii) consisting of water and uncombined mixture of hydrogen and oxygen. System (iii) however is not homogeneous in chemical composition because in the upper part of the system hydrogen and oxygen are present in the ratio 1:1 where as in the bottom portion they are present in the ratio 2:1.

System (i) also satisfies condition (ii), because both hydrogen and oxygen have combined chemically in every part of the system. System (ii) on the other hand does not satisfies condition (ii) because the bottom part of the system has two elements namely hydrogen and oxygen have chemically combined where as in the upper part of the system the (ii) elements appear as a mixture of two individual gases.

Invariable in chemical aggregation means that the state of chemical combination of the system should not change with time. Thus the mixture of hydrogen and oxygen, if it is changing into steam during the time the system was under consideration, then the systems chemical aggregation is varying with time and hence this system is not a pure substance. Thus the system (i) is a pure substance where as the systems (ii) and (iii) are not pure substances.

Specific heat, C

When interaction of heat takes place between a closed system and its surroundings, the internal energy of the system changes. If δQ is the amount of heat transferred to raise the temperature of 1 kg of substance by dT, then, specific heat $C = \delta Q/dT$

As we know, the specific heat of gas depends not only on the temperature but also upon the type of the heating process. i.e., specific heat of a gas depends on whether the gas is heated under constant volume or under constant pressure process.

We have $dQ = m\,C_V.\,dT$ for a rev. non-flow process at constant volume

and $dQ = m\,C_p.\,dT$ for a rev. non-flow process at constant pressure

For a perfect gas, C_p & C_V are constant for any one gas at all pressure and temperatures. Hence, integrating above equations.

Flow of heat in a rev. constant pressure process = $m\,C_p\,(T_2 - T_1)$

Flow of heat in a rev. constant volume process = $m\,C_V\,(T_2 - T_1)$

The internal energy of a perfect gas is a function of temperature only. i.e, u = f (T), to evaluate this function, let 1 kg of gas be heated at constant volume

From non-flow energy equation, $\delta Q = dU + \delta W$

$\delta W = 0$ since volume remains constant

$\delta Q = dU = C_V.\,dT$

$\therefore$

Int. $U = C_V T + k$ where k is a constant

Enthalpy: Consider a system undergoing a quasi equilibrium constant pressure process. We have from 1st law of thermodynamics for a non-flow process,

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

$$W_{1\text{-}2} = \int_1^2 p dv$$

Since pressure is constant $W_{1\text{-}2} = p\ (V_2 - V_1)$

$$\therefore Q_{1\text{-}2} = U_2 - U_1 + p\ (V_2 - V_1)$$

$$= (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

i.e., heat transfer during the process is given in terms of the change in the quantity (U + pV) between initial and final states. Therefore, it find more convenient in thermodynamics to define this sum as a property called Enthalpy (H)

i.e., $H = U + pV$

In a constant pressure quasi equilibrium process, the heat transfer is equal to the change in enthalpy which includes both the change in internal energy and the work for this particular process.

The enthalpy of a fluid is the property of the fluid, since it consists of the sum of a property and the product of the two properties. Since enthalpy is a property, like internal energy, pressure, specific volume and temperature, it can be introduced into any problem whether the process is a flow or a non-flow process.

For a perfect gas, we have $h = u + pV$

$$= C_V\ T + RT$$

$$= (C_V + R)\ T$$

$$= C_pT$$

i.e., $h = C_pT$ & $H = mC_pT$

For any process, $\delta Q = dH$

$$= mC_pdT$$

$\therefore$ For a process between states 1 & 2

Change in enthalpy $= (H_2 - H_1) = mC_p\ (T_2 - T_1)$

Specific heat at Constant Volume: When heat interaction takes place at constant volume, δW = 0 and from 1st law of thermodynamics, for unit mass, $(\delta q)_V = dU$ The amount of heat supplied or removed per degree change in temperature, when the system is kept under constant volume, is called as the specific heat at constant volume,

$$\text{Or} \qquad C_V = \left[\frac{\delta Q}{dT}\right]_V \cong \left[\frac{dU}{dT}\right]_V$$

$$\text{Or } dU = C_V\, dT$$

Specific heat at Constant pressure When heat interaction is at constant pressure, $(\delta q)_p = dh$ The amount of heat added or removed per degree change in temperature, when the system is kept under constant pressure, is called as the specific heat at constant pressure.

$$\text{Or } C_p = \left[\frac{\delta Q}{dT}\right]_p \cong \left[\frac{dh}{dT}\right]_p$$

$$\text{Or } dh = C_p.\, dT$$

Application of 1st law of thermodynamics to non-flow or closed system: **a) Constant volume process (V = constant)**

Applying 1st law of thermodynamics to the process,

system: a) Constant volume process (V = constant)

Applying 1st law of thermodynamics to the process,

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

$$= U_2 - U_1 + 0$$

$$\text{i.e., } Q_{1\text{-}2} = C_V\,(T_2 - T_1)$$

For mass "m" of a substance, Q = mCV (T2 – T1)

b) Constant pressure (p = Constant)

Applying 1st law of thermodynamics to the process,

$Q_{1-2} = u_2 - u_1 + W_{1-2}$

The work done, $W_{1-2} = \int_1^2 p\, dV = p\,(V_2 - V_1)$

i.e., $Q_{1-2} = u_2 - u_1 + p\,(V_2 - V_1) = (u_2 + pV_2) - (u_1 + pV_1)$

$= h_2 - h_1$

i.e., $Q = C_p\,(T_2 - T_1)$

For mass 'm' of a substance, $Q = mC_p\,(T_2 - T_1)$

c) Constant temperature process (Isothermal process, T = constant)

Applying 1st law of thermodynamics to the process,

Q1-2 = U2 – U1 + W1-2

$= C_V\,(T_2 - T_2) + W_{1-2}$

i.e., $Q_{1-2} = W_{1-2} \quad \because T_1 = T_2$

$Q_{1-2} = p_1V_1 \ln V_2/V_1$

$= p_1\, V_1 \ln p_1/p_2$

The above equation is true for an adiabatic process whether the process is reversible or not. In an adiabatic experiment, the work done W_{1-2} by the fluid is at the expense of a reduction in the internal energy of the fluid. Similarly in an adiabatic composition process, all the work done on the fluid goes to increase the internal energy of the fluid.

To derive $pV^{\gamma} = C$: For a reversible adiabatic process

We have δq = du + δu

For a reversible process, δw = p dV

$\therefore \delta q = du + p\, dV$

$= O \because$ For an adiabatic process $\delta q = 0$

Also for a perfect gas, $pV = RT$ or $p = \dfrac{RT}{V}$

$\therefore dU + RT\,\dfrac{dV}{V}$

Also, $u = C_V T$ or $du = C_V dT$

$$\therefore C_V dT + RT\frac{dV}{V}$$

$$\text{or } C_V\frac{dT}{T} + R\frac{dV}{V} = 0$$

Int., $C_V \ln T + R \ln V = \text{constant}$

Sub. $T = pV/R$

$$C_v \ln\frac{Pv}{R} + R\ln v = \text{constant}$$

$$\text{Or } \ln\frac{pV}{R} + \frac{R}{C_V}\ln V = \text{constant}$$

$$\text{Also, } C_V = \frac{R}{\gamma - 1}\ or\ \frac{R}{C_V} = \gamma - 1$$

$$\therefore \ln\frac{pV}{R} + (\gamma - 1)\ln V = \text{constant}$$

$$\therefore \ln\frac{pV}{R} + \ln V^{\gamma-1} = \text{constant}$$

$$\text{or } \ln\frac{pVxV^{\gamma-1}}{R} = \text{constant}$$

$$\text{i.e., } \ln\frac{pV^{r}}{R} = \text{constant}$$

$$\text{or } \frac{pV^{r}}{R} = e^{\text{constant}} = \text{constant}$$

i.e., $pV^{\gamma} = \text{constant}$

we have $pV = RT$

or $p = \frac{RT}{V}$

sub. This value of p in $pV^{\gamma} = C$

$$\frac{RT}{V} V^{\gamma} = C \qquad \text{or } TV^{\gamma-1} = \text{constant} \qquad \text{--- (a)}$$

Also, $V = \frac{RT}{P}$ sub. This in equation pressure$^{\gamma}$ = C

$$p\left(\frac{RT}{p}\right)^{\gamma} = \text{constant}$$

$$\therefore \frac{T^2}{p^{\gamma-1}} = \text{constant} \qquad \text{or} \quad \frac{T}{p^{\left(\frac{\gamma-1}{\gamma}\right)}} = \text{constant} \qquad \text{--- (b)}$$

$\therefore$ For a reversible adiabatic process for a perfect gas between states 1 & 2, we can write

$$p_1V_1^{\gamma} = p_2V_2^{\gamma} \qquad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{r} \qquad \text{--- (c)}$$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \text{--- (d)}$$

$$\frac{T_1}{p_1^{r-1/r}} = \frac{T_2}{p_2^{r-1/r}} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{r-1}{r}} \qquad \text{--- (e)}$$

The work done in an adiabatic process is $W = u_1 - u_2$

The gain in I.E. of a perfect gas, is $u_2 - u_1 = C_V (T_2 - T_1)$

$$W = C_V (T_1 - T_2)$$

But $C_V = \frac{R}{\gamma - 1}$

$$\therefore W = \frac{R(T_1 - T_2)}{\gamma - 1}$$

Using $pV = RT$, $W = \frac{p_1V_1 - p_2V_2}{\gamma - 1}$

1. A cylinder contains 0.45 m^3 of a gas at 1 bar & 80^0C. The gas is compressed to a volume of 0.13 m^3, the final pressure being 5 bar. Determine i) the mass of the gas, ii) the value of index 'n' for composition, iii) the increase in internal energy of the gas and iv) the heat received or rejected by the gas during compression. (Take $\gamma = 1.4$, $R = 294.2$ J/kg-K).

Solution: $V_1 = 0.45\ m^3$ $p_1 = 1 \times 10^5$ Pa $V_2 = 0.13\ m^3$ $T_1 = 353$ K

$p_2 = 5 \times 10^5$ Pa

i) We have $p_1V_1 = mRT_1 \therefore m = \frac{1x10^5 x0.45}{294.2x353} = 0.433$ kg

ii) $p_1V_1^n = p_2V_2^n$ i.e., $\left(\frac{V_1}{V_2}\right)^n = \frac{p_2}{p_1}$

$$\text{Or } \left(\frac{0.45}{0.13}\right)^n = \left(\frac{5}{1}\right) \qquad \therefore n = 1.296$$

iii) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1} = \left(\frac{0.45}{0.13}\right)^{0.296} \qquad \therefore T_2 = 509.7$ K

$\therefore$ Increase in int. energy, $\Delta U = mC_v\ (T_2 - T_1)$

$$= 0.433 \text{ x } \frac{R}{r-1}(T_2 - T_1)$$

2. A fluid system consisting of 4.17 kg of a pure substance has an energy E of 85 kJ. The kinetic energy of the system is 17 kJ and its gravitational potential energy is 5 kJ. The system undergoes an adiabatic process in which the final sp. i.e., is 150 kJ/kg, the final kinetic energy is 1.9 kJ and the final gravitational potential energy is 1.1 kJ. The effects due to electricity, capillary and magnetism are assumed to be absent. a) Evaluate the initial value of the sp. i.e., of the fluid. b) Determine the magnitude and sign of the work done during the process.

Solution: Total initial energy $E_1 = KE_1 + PE_1 + U_1$

$$85 = 17 + 5 + U_1 \therefore U_1 = 63 \text{ kJ}$$

$$\therefore \text{Initial sp. i.e.,} = \frac{63}{4.17} = 15.108 kJ/kg$$

Final state: $E_2 = k\varepsilon_2 + P\varepsilon_2 + U_2 = 1.9 + 1.1 + 4.17\ (150) = 628.5$ kJ

From 1st law, $\delta Q = E_2 - E_1 + W$

$$0 = 628.5 - 63 + \therefore W = -565.5 \text{ kJ}$$

A mass of 0.2 kg of a pure substance at a pressure of 1 bar and a temperature of 313 k occupies a volume of 0.15 m^3. Given that the int. energy of the substance is 31.5 kJ, evaluate the sp. Enthalpy of the substance.

Solution: $m = 0.2$ kg $P = 1 \times 10^5$ N/m^2 $T = 313$ k $v = 0.15$ $v = 31.5$ kJ

We have, enthalpy = U + Pv

$= 31.5 \times 10^3 + 1 \times 10^5 \times 0.15$

$= 46.5$ kJ

$\therefore$ sp. Enthalpy = 46.5/0.2 = 232.5 kJ/kg

3. A gas enters a system at an initial pressure of 0.45 MPa and flow rate of 0.25 m^3/s and leaves at a pressure of 0.9 MPa and 0.09 m^3/s. During its passage through the system the increase in i.e., is 20 kJ/s. Find the change of enthalpy of the medium.

Solution: $p_1 = 0.45 \times 10^6$ Pa $V_1 = 0.25\ m^3/s$

$p_2 = 0.9 \times 10^6$ Pa $V_2 = 0.09\ m^3/s$

$(u_2 - u_1) = 20 \times 10^3$ J/s

We have from 1st law for a constant pressure quasi static process

$Q_{1-2} = (u_2 + p_2V_2) - (u_1 + p_1V_1)$

$= (H_2 - H_1)$

= Change in enthalpy

$= (u_2 - u_1) + p_2V_2 - p_1V_1$

$= 20 \times 10^3 + 0.9 \times 10^6 \times 0.09 - 0.45 \times 10^6 \times 0.25$

$(H_2 - H_1) = -\ 11.5$ kJ/s

$\therefore$ There is a decrease in enthalpy during the process

MODULE-4

THERMODYNAMIC RELATIONS

Ideal Gas

Definition: A substance is said to be an ideal gas if it satisfies the following equations

i.e., $Pv = RT$ and $u = f(T)$

Where P is the pressure exerted by the substance, v is the specific volume of the substance, T is the temperature in degree Kelvin, u is the specific internal energy and R is the gas constant. Experience has shown that almost all real gases satisfy the above equations over wide ranges of pressures and temperatures. However there are certain situations where the real gases cannot be treated as ideal gases.

Mole of a Gas

A mole of a gas is that quantity of gas whose mass is numerically equal to its molecular weight. For example, 1 kg mol of hydrogen is equal to 2 kg, has molecular weight of hydrogen is 2. Therefore if n is the total number of moles, m is mass and M is the molecular weight then, $nM=m$

Avogadro's Hypothesis

Avogadro‟s law states that equal volumes of all gases measured at the same temperature and pressure contain the same number of moles.

Consider two gases A and B. The law states that if $V_A = V_B$, $T_A = T_B$ and $P_A = P_B$ then $n_A = n_B$

For gas A, the equation of state can be written as $P_A V_A = m_A R_A T_A = n_A M_A R_A T_A$

Where *R* is called the universal gas constant and R is called the characteristic gas constant. The value of *R* =8.3143 kJ/kgmol-K.

The ideal gas equation can also be written in terms of *R* as PV = nMRT = n *R* T where *R* = R/M as u and h are functions of temperature.

From the above equations, $du = c_V\, dT$ and $dh = c_P\, dT$

For a mass of m kg of gas the equations become

$dU = m\, c_V\, dT$ and $dH = m\, c_P\, dT$ On integrating we get

$$U_2 - U_1 = m\int_{T_1}^{T_2} c_v\,dT$$

$$and\ H_2 - H_1 = m\int_{T_1}^{T_2} c_p\,dT$$

Relation between specific heats for an ideal gas

For an ideal gas h = u + RT

Therefore $\frac{dh}{dT} = \left(\frac{du}{dT}\right) + R$

Or $c_P = c_V + R$

ie, $c_P - c_V = R$

Dividing the above equation by c_V, we get

$$\gamma - 1 = \frac{R}{c_V}$$

$$Or\ c_V = \frac{R}{\gamma - 1}$$

Similarly, dividing the above equation by c_P, we get

$$c_P = \frac{\gamma R}{\gamma - 1}$$

Work done by a perfect gas during a reversible adiabatic process in a closed system:

From the first law of TD,

For an adiabatic process, δq=0

Hence the work done by a unit mass of a perfect gas on a piston during an adiabatic expansion process is equal to the decrease in internal energy, i.e., δw = -du

Whereas, for an adiabatic compression process, the internal energy of the gas will increase with a consequent increase in temperature.

For a perfect gas, du=c_vdT

$$\therefore \delta w = -c_v dT$$

$$But, c_v = \frac{R}{\gamma - 1} \quad \therefore \delta w = -\frac{R}{\gamma - 1} dT$$

$$= \frac{P_1 v_1 - P_2 v_2}{\gamma - 1}$$

$$= \frac{P_1 v_1}{\gamma - 1}\left[1 - \frac{P_2 v_2}{P_1 v_1}\right]$$

$$= \frac{P_1 v_1}{\gamma - 1}\left[1 - \left(\frac{P_1}{P_2}\right)^{\frac{\gamma - 1}{\gamma}}\right]$$

The polytropic process of a perfect gas:

A Polytropic process is one for which the pressure volume relation is given by pv^n = constant, where the exponent n for the given process is a constant and may have any numerical value ranging from plus infinity to minus infinity.

From the above equation, it is evident that the properties at the end states of the reversible or irreversible polytropic process of a perfect gas may be written in the form

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^n$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} = \left(\frac{v_2}{v_1}\right)^{n-1}$$

There are four values of the exponent n that indicate processes of particular interest. When

- n = 0, constant pressure or isobaric process
- n = ± ∞, constant volume or isovolumic process
- n = 1, constant temperature or isothermal process
- n = γ constant entropy or isentropic process

These processes are shown in the fig. on p-v and T-s diagrams.

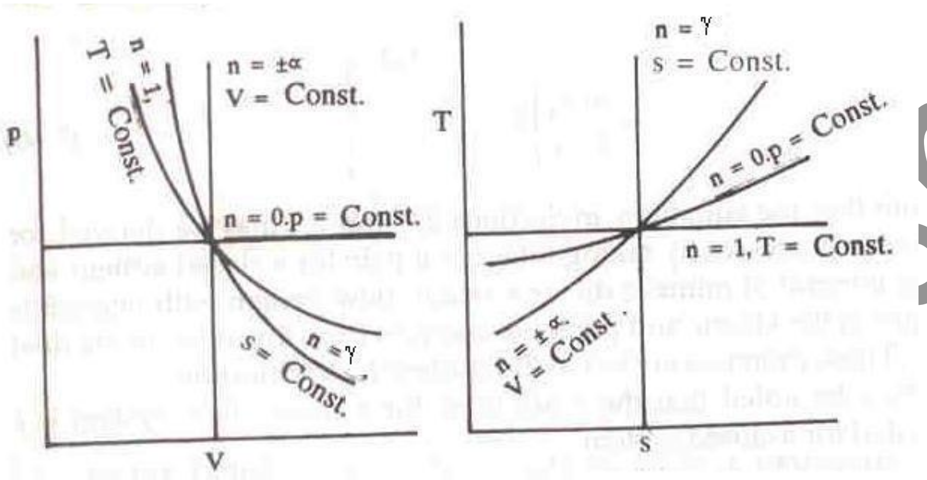


Figure: Polytropic Process on p-v and T-s diagrams

Work done and heat transfer by a perfect gas during a polytropic process:

For the closed system, the work done during a polytropic expansion process is given by,

$$w_{1-2} = \int_1^2 p\,dv = \frac{R}{n-1}(T_1 - T_2)$$

$$= \frac{P_1 v_1 - P_2 v_2}{n-1}$$

$$= \frac{P_1 v_1}{n-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right]$$

The work done for a steady flow system during a polytropic expansion process is given by,

$$\frac{n\,P_1 v_1}{n-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right]$$

i) The heat transfer for a closed system:

From the first law of thermodynamics for a unit mass of substance

$\delta q = \delta w + du$

Since $du = c_v dT$ and

for a reversible process

$\delta w = p dv$

$\delta q = c_v dT + p dv$

ii) The heat transfer in a steady flow process:

From the first law for steady flow system for a unit mass of fluid

$\delta q = \delta w + dh$ But $dh = c_p dT$ and

for a reversible steady flow process

$\delta w = -v dp$

Therefore $\delta q = c_p dT - v dp$

Change in Entropy

Let P_1, v_1, T_1, S_1 apply to the initial conditions of certain amount of gas. P_2, v_2, T_2, S_2, apply to the final conditions after adding some heat.

From first law of TD, $\delta q = \delta w + du$

$$\delta q = P.dv + du$$

Also by definition, $du = c_v\, dT$

Therefore $\delta q = P.dv + c_v dT$

Evaluation of change in entropy in various quasi static processes

1. Constant Volume Process

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

$\delta W = 0$ for a constant volume process. Therefore heat added, $\delta Q = dU = m\, c_v\, dT$

Divide by T

$$\frac{\delta Q}{T} = mc_v \frac{dT}{T}$$

$$\text{Integrating, } \int_1^2 \frac{\delta Q}{T} = \int_1^2 mc_v \frac{dT}{T}$$

$$\therefore S_2 - S_1 = mc_v.\ln\frac{T_2}{T_1}$$

2. Constant Pressure Process

$\delta Q = \delta W + dU$

$= P.dv + dU$

$= m\,R\,dT + mc_v\,dT$

$= m\,(R + c_v)\,dT$

$= m\,(c_P - c_v + c_v)dT$

$= mc_P\,dT$

Divide by T, $\frac{\delta Q}{T} = mc_P\frac{dT}{T}$

Integrating, $\int_1^2\frac{\delta Q}{T} = \int_1^2 mc_P\frac{dT}{T}$

$$\therefore S_2 - S_1 = mc_P.\ln\frac{T_2}{T_1}$$

3. Isothermal Process

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

But $dU = 0$

$$\therefore \delta Q = P_1v_1\ln\frac{v_2}{v_1}$$

Divide by T, $\frac{\delta Q}{T} = \frac{mRT_1}{T_1}\ln\frac{v_2}{v_1}$

Integrating we get, $S_2 - S_1 = mR\ln\frac{v_2}{v_1}$

4. Reversible Adiabatic Process

$\delta Q = 0$

Therefore $S_2 - S_1 = 0$

Hence the process is called isentropic process

Divide by T, $\frac{\delta Q}{T} = \frac{\gamma - n}{\gamma - 1} \frac{P.dv}{T}$

$$\therefore \int_1^2 \frac{\delta Q}{T} = \frac{\gamma - n}{\gamma - 1} \int_1^2 P \frac{dv}{T}$$

We know Pv = RT, i.e., P = RT/v

$$S_2 - S_1 = \frac{\gamma - n}{\gamma - 1} \int_1^2 \frac{RT}{v} \frac{dv}{T}$$

$$= \frac{\gamma - n}{\gamma - 1} R \int_1^2 \frac{dv}{v}$$

$$\therefore S_2 - S_1 = \frac{\gamma - n}{\gamma - 1} R . \ln \frac{v_2}{v_1}$$

Semi-perfect gas:

It can be observed that from the definition of c_p and c_v that the specific heats can be either constants or functions of temperature.

A semi-perfect gas is one which follows the ideal gas relation with its specific heats being functions of temperature.

i.e., Pv = RT

$c_p = \Phi(T)$

$c_v = f(T)$

1. 1.25 m^3 of air at 180 ^{0}C at 8 bar is undergoing a constant pressure until the volume is doubled. Determine the change in the entropy and enthalpy of air.

Solution: Assuming air behaves like a perfect gas we have, $C_P = 1.005$ kJ/kg ^{0}K,

$C_V = 0.718$ kJ/kg ^{0}K and $R = 0.287$ kJ/kg ^{0}K

Given: $V_1 = 1.25\ m^3$, $T_1 = 180 + 273 = 453^0$ K, $P_1 = P_2 = 8 \times 10^5 N/m^2$ and $V_2 = 2V_1$

For a constant pressure process, change in entropy is

$$S_2 - S_1 = mC_P \ln\left(\frac{T_2}{T_1}\right)$$

We have $P_1V_1 = mRT_1$

$$\therefore m = \frac{8x10^5\, x1.25}{287x453} = 7.69kg$$

$$Also \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore T_2 = \frac{2x1.25x453}{1.25} = 906^0\ K$$

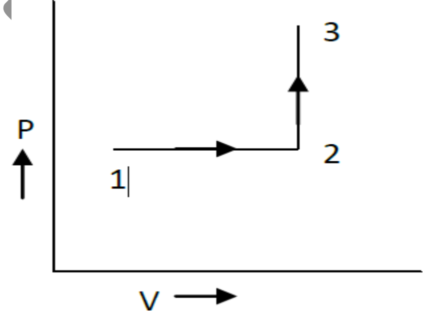
Therefore change in entropy $= 7.69x1.005\ln\frac{906}{453}$

$= 5.596$ kJ/^{0}K

Change in enthalpy $= Q_{1\text{-}2} = mC_P\,(T_2 - T_1) = 3500.99$ kJ

2. 1kg of air initially at 27^{0}C is heated reversibly at constant pressure until the volume is doubled, and then is heated at constant volume until the pressure is doubled. For the total path find i) Work transfer, ii) Heat transfer, iii) Change in entropy

Solution: Given: m = 1 kg, $T_1 = 300^0$ K $V_2 = 2V_1$, $P_3 = 2P_2 = 2P_1$



Process 1-2: Constant pressure process

i) Work done, $W_{1-2} = P (V_2 – V_1)$

$= PV_2 – PV_1$

$= mR (T_2 – T_1)$

Also $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

But $P_1 = P_2$ $\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2}$ But $V_2 = 2V_1$

Therefore $T_2 = 2T_1 = 600^0K$

Therefore work done $W_{1-2} = 1 \times 0.287 \times (600 – 300)$

$= 86.1$ kJ

ii) From first law of TD, Heat Transfer, $Q_{1-2} = W_{1-2} + (U_2 – U_1)$

$= W_{1-2} + mC_v (T_2 – T_1)$

$= 86.1 + 1 \times 0.718 \times (600 – 300)$

$= 301.5$ kJ

iii) Change in entropy, $S_2 - S_1 = mC_P \ln\frac{T_2}{T_1}$

$$= 1(1.005)\ln\frac{600}{300}$$

$= 0.6966$ kJ/^{0}K

Process 2-3: Constant Volume Process

Given, $P_3 = 2P_2$, $T_2 = 600$ K

We have $\frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3}$ But $V_2 = V_3$

$$\therefore T_3 = \frac{T_2P_3}{P_2} = \frac{T_2 x 2P_2}{P_2}$$

$= 2 \times T_2 = 1200^0K$

i) Work done, $W_{2-3} = 0$

ii) Heat transfer, $Q_{2-3} = W_{2-3} + (U_3 - U_2)$

$= mC_v (T_3 - T_2)$

$= 430.8$ kJ

iii) Change in entropy $S_3 - S_2 = mC_P \ln \frac{T_3}{T_2}$

$= 0.4977$ kJ/^{0}K

Therefore work transfer in total path, $W_{1-3} = W_{1-2} + W_{2-3}$

$= 86.1 + 0$

$= 86.1$ kJ

Heat transfer in total path, $Q_{1-3} = Q_{1-2} + Q_{2-3}$

$= 301.5 + 430.8$

$= 732.3$ kJ

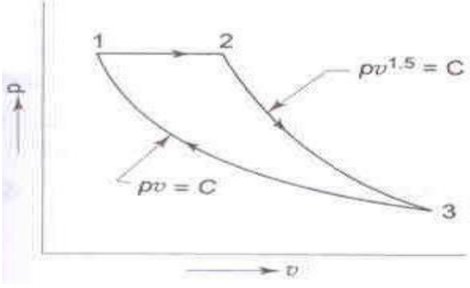
Change in entropy for the total path $= (S_3 - S_1) = (S_3 - S_2) + (S_2 - S_1)$

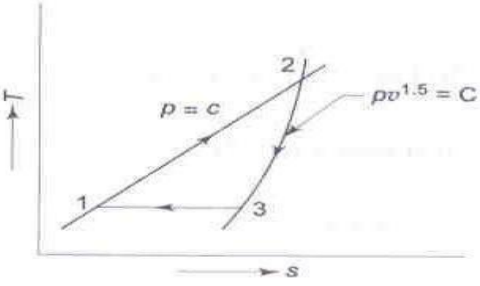
$= 0.4977 + 0.6966$

$= 1.1943$ kJ/^{0}K

3. A mass of air is initially at 260^{0}C and 700 kPa, and occupies 0.028m^3. The air is expanded at constant pressure to 0.084m^3. A polytropic process with n = 1.5 is then carried out, followed by a constant temperature process which completes a cycle. All the processes are reversible. (i) sketch the cycle in the P-v and T-s diagrams. (ii) find the heat received and heat rejected in the cycle.(iii) find the efficiency of the cycle.

Solution: $P_1 = 700$ kPa, $T_1 = 533K = T_3$, $V_1 = 0.028m^3$, $V_2 = 0.084m^3$





We have $P_1V_1 = mRT_1$

$$\therefore m = \frac{700x0.028}{0.287x533} = 0.128kg$$

$$Now \quad \frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \frac{0.084}{0.027} = 3$$

Therefore $T_2 = 3 \text{ x } 533 = 1559$ K

Heat transfer in process 1-2, $Q_{1-2} = mc_p (T_2 – T_1)$

$= 0.128 \text{ x } 1.005 (1599 – 533)$

$= 137.13$kJ

For process 3-1

$Q_{3-1} = dU + W_{3-1}$

On substituting, $Q_{3-1} = - 64.53$ kJ

Heat received in the cycle 137.13 kJ

Heat rejected in the cycle $Q_2 = 19.59 + 64.53 = 84.12$ kJ

4. 1 kg of air at a pressure of 7 bar and a temperature of 90^0C undergoes a reversible polytropic process which may be represented by $PV^{1.1} = C$, final pressure is 1.4 bar. Evaluate i) The final specific volume, temperature and increase in entropy, ii) Work done and heat transfer.

Solution: Given, m = 1 kg, P_1 = 7 bar, $T_1 = 363^0K, PV^{1.1} = C$, P_2 = 1.4 bar

Air is perfect gas i.e., $P_1V_1 = mRT_1$

$$\therefore v_1 = \frac{1(287)(363)}{7x10^5} = 0.14883m^3 / kg$$

Also we have, $P_1V_1^{1.1} = P_2V_2^{1.1}$

Therefore $V_2 = 0.6429$ m^3

Also $P_2V_2 = mRT_2$

Therefore $T_2 = 313.61^0K$

Change in entropy for a polytropic process is,

Substituting the values, noting $\gamma = 1.4$ and R = 0.287 kJ/kg^{0}K, we get

$S_2 - S_1 = 0.31495 kJ/kg^0K$

Work done, $W_{1-2} = \frac{P_1V_1 - P_2V_2}{n-1}$

Substituting we get, $W_{1-2} = 141.75$ kJ/kg

Heat transfer $Q_{1-2} = W_{1-2} + (U_2 - U_1)$

$= W_{1-2} + mC_v (T_2 - T_1)$

$= 141.75 - 35.462$

$= 106.29$ kJ/kg

MODULE-5

IDEAL GAS MIXTURE

Thermodynamics of Non-reactive Mixtures

Assumptions:

1. Each individual constituent of the mixture behaves like a perfect gas.
2. The mixture behaves like a perfect gas.
3. Individual constituents do not react chemically when the mixture is undergoing a process.

Mixture characteristics:

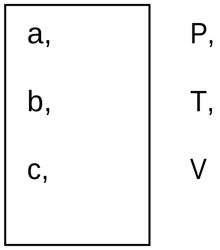


Figure: Homogeneous gas mixture

Consider a mixture of gases a, b, c, …. existing in equilibrium at a pressure P, temperature T and having a volume V as shown in figure.

The total mass of the mixture is equal to the sum of the masses of the individual gases,

i.e., $m_m = m_a + m_b + m_c + \ldots\ldots$ where subscript m = mixture, a, b, c = individual gases.

Mass fraction: The mass fraction of any component is defined as the ratio of the mass of that component to the total mass of the mixture. It is denoted by m_f.

$$Thus,\quad m_{fa} = \frac{m_a}{m},\quad m_{fb} = \frac{m_b}{m},\quad m_{fc} = \frac{m_c}{m}$$

$$\therefore m_{fa} + m_{fb} + m_{fc} + \ldots.. = \sum_i m_{f_i} = 1$$

Where the subscript i stands for the ith component. It shows that the sum of the mass fraction of all components in a mixture is unity.

Mole fraction: If the analysis of a gas mixture is made on the basis of the number of moles of each component present, it is termed a molar analysis. The total number of moles for the mixture is equal to the sum of the number of moles of the individual gases i.e., $n_m = n_a + n_b + n_c + \ldots\ldots..$ where subscript m = mixture, a, b, c = individual gases.

(A mole of a substance has a mass numerically equal to the molecular weight of the substance, i.e., 1 kg mol of O_2 has a mass of 32 kg, 1 kg mol of N_2 has a mass of 28 kg, etc.,)

The mole fraction of any component is defined as the ratio of the number of moles of that component to the total number of moles. It is denoted by y

$$i.e.,\quad y_a = \frac{n_a}{n_m},\ y_b = \frac{n_b}{n_m},\ y_c = \frac{n_c}{n_m}$$

$$and\quad \therefore\quad y_a + y_b + y_c + \ldots\ldots = \sum_i y_i = 1$$

i.e., the sum of the mole fraction of all components in a mixture is unity.

The mass of a substance m is equal to the product of the number of moles n and the molecular weight (molar mass) M, or m = nM

$\therefore$ For each of the components we can write,

$$n_m M_m = n_a M_a + n_b M_b + n_c M_c + \ldots\ldots$$

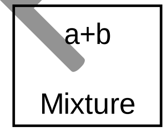
Where M_m is the average molar mass or molecular weight of the mixture.

Or $M_m = y_a M_a + y_b M_b + y_c M_c$

Thus, the average molecular weight of a gas mixture is the sum of the products of all the components of the mole fraction and corresponding molecular weight of each component.

Note: Universal gas constant R MR where M = molecular weight, R: specific gas constant, and R =8.3143 kJ/kg-mole K

Partial Pressure:



P, T,

a & b = gases of the mixture

V = Total volume of the mixture

T = Temperature of the mixture

Partial pressure of a constituent in a mixture is the pressure exerted when it alone occupies the mixture volume at mixture temperature. If P_a is partial pressure of gas „a", then $P_aV = m_aR_aT$

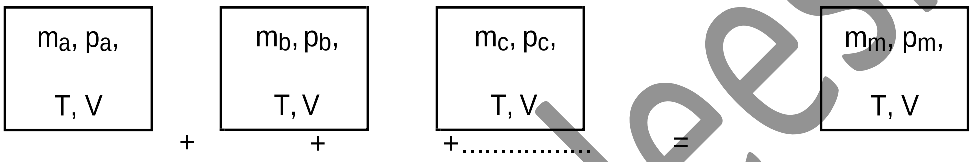
Where m_a = mass of gas „a‟, R_a = gas constant for gas „a‟, similarly $P_bV = m_bR_bT$

Partial Volume: Partial volume of a gas in a mixture is the volume occupied by the gas component at mixture pressure and temperature. Let V_a = partial volume of gas „a" and V_b = partial volume of gas „b‟.

i.e., $PV_a = m_aR_aT$ & $PV_b = m_bR_bT$

The Gibbs-Dalton Law

Consider a mixture of gases, each component at the temperature of the mixture occupying the entire volume occupied by the mixture, and exerting only a fraction of the total pressure as shown in figure.



Applying the equation of state for this mixture we may write,

$$P_m V = m_m R_m T = n_m M_m R_m T = n_m \bar{R} T$$

$$\text{Similarly} \quad p_aV = n_a\bar{R}T$$

$$p_bV = n_b\bar{R}T$$

$$p_cV = n_c\bar{R}T$$

The above equation is known as the Gibbs Dalton Law of partial pressure, which states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the individual components, if each component is considered to exist alone at the temperature and volume of the mixture.

Gas constant for the mixture:

We have $P_aV = m_aR_aT$

$P_bV = m_bR_bT$

Or $(P_a + P_b) V = (m_aR_a + m_bR_b) T$

Also, since the mixture behaves like a perfect gas,

We have $PV = mRT$ --- (1)

By Dalton‟s law of partial pressure, which states that, the pressure of mixture of gas is equal to the sum of the partial pressures of the individual components, if each component is considered to exist alone at the temperature and volume of the mixture.

i.e., $P = P_a + P_b$

The Amagat-Leduc Law: Expresses the law of additive volume which states that the volume of a mixture of gases is equal to the sum of the volumes of the individual components at the pressure and temperature of the mixture.

., $V_m = V_a + V_b + V_c \ldots_{P,\,T} = \sum V_i$

For Dalton law, $P_m = P_a + P_b + P_c + \ldots_{V,\,T} = \sum P_i$

Gibb's Law: It states that the internal energy, the enthalpy and the entropy of a mixture of gas is equal to sum of the internal energies, the enthalpies and entropies respectively of the individual gases evaluated at mixture temperature and pressure.

$\therefore U = U_a + U_b$

$mU = m_a U_a + m_b U_b$

$U = m_{fa} U_a + m_{fb} U_b$

$$\frac{dU}{dT} \quad m_{fa} \frac{dU_a}{dT} \quad m_{fb} \frac{dU_b}{dT} \quad C_V$$

Similarly $C_P = m_{fa} (C_p)_a + m_{fb} (C_p)_b$

An ideal gas is a gas having no forces of intermolecular attraction. The gases which follow the gas laws at all range of pressures and temperatures are considered as „ideal gases‟. An ideal gas obeys the perfect gas equation Pv = RT and has constant specific heat capacities.

A real gas is a gas having forces of inter molecular attraction. At very low pressure relative to the critical pressure or at very high temperatures relative to the critical temperature, real gases behave nearly the same way as a perfect gas. But since at high pressure or at low temperatures the deviation of real gases from the perfect gas relation is appreciable, these conditions must be observed carefully, otherwise errors are likely to result from inappropriate application of the perfect gas laws.

Due to these facts, numerous equations of state for real gas have been developed, the derivation of which is either analytical, based on the kinetic theory of gases, or empirical, derived from an experimental data.

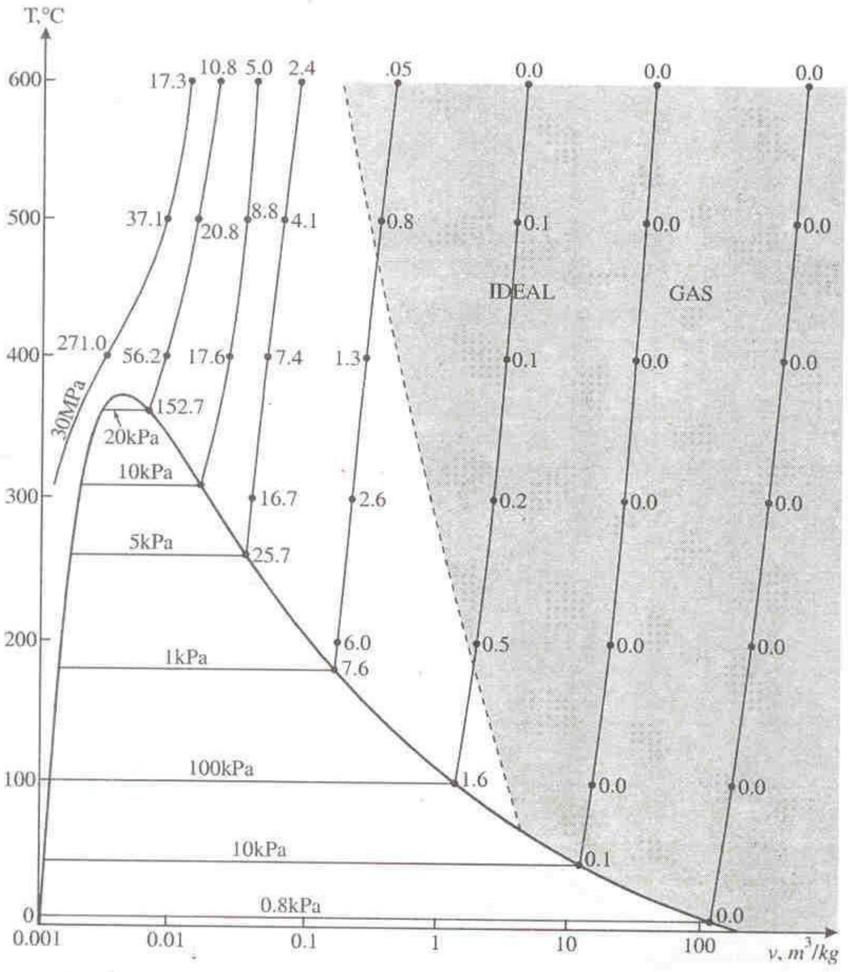


Figure:Percentage of error ($[\,|v_{table} - v_{ideal}|/v_{table}] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal ges with less than 1 percent error.

Vander Waals' Equation of State:

In deriving the equation of state for perfect gases it is assumed that the volume occupied by the molecules of the gas in comparison to the volume occupied by the gas and the force of attraction between the adjacent molecules is very small and hence the molecules of gas are neglected. At low pressures, where the mean free path is large compared to the size of the molecules, these assumptions are quite reasonable. But at high pressure, where the molecules come close to each other, these are far from correct. Vander waals‟ equation introduces terms to take into account of these two modifying factors into the equation of state for a perfect gas.

The Vander Waals' equation of state is given by,

$$or \quad P \qquad \frac{RT}{v \quad b} \quad \frac{a}{v^2}$$ P = Pressure v = Volume/unit mass R = gas constant

where a and b are constants for any one gas, which can be determined experimentally, the constants account for the intermolecular attractions and finite size of the molecules which were assumed to be non-existent in an ideal gas. The term accounts for the intermolecular forces i.e, force of cohesion and the term b was introduced to account for the volume occupied by the molecules i.e., co-volume. 2 va

Determination of Van der Waals constants in terms of critical properties

The determination of two constants a and b in the Van der Waals equation is based on the fact that the critical isotherm on a p-v diagram has a horizontal inflexion point at the critical point. Therefore the first and second derivative of P with respect v at the critical point must be zero.

Compressibility Factor and Compressibility Chart:

The specific volume of a gas becomes very large when the pressure is low or temperature is high. Thus it is not possible to conveniently represent the behaviour of real gases at low pressure and high temperature.

For a perfect gas, the equation of state is Pv = RT. But, for a real gas, a correction factor has to be introduced in the perfect gas to take into account the deviation of the real gas from the perfect gas equation. This factor is known as the compressibility factor, Z and is defined as,

$$Z = \frac{Pv}{RT}$$

Z = 1 for a perfect gas. For real gases the value of Z is finite and it may be less or more than unity depending on the temperature and pressure of the gas.

Reduced Properties:

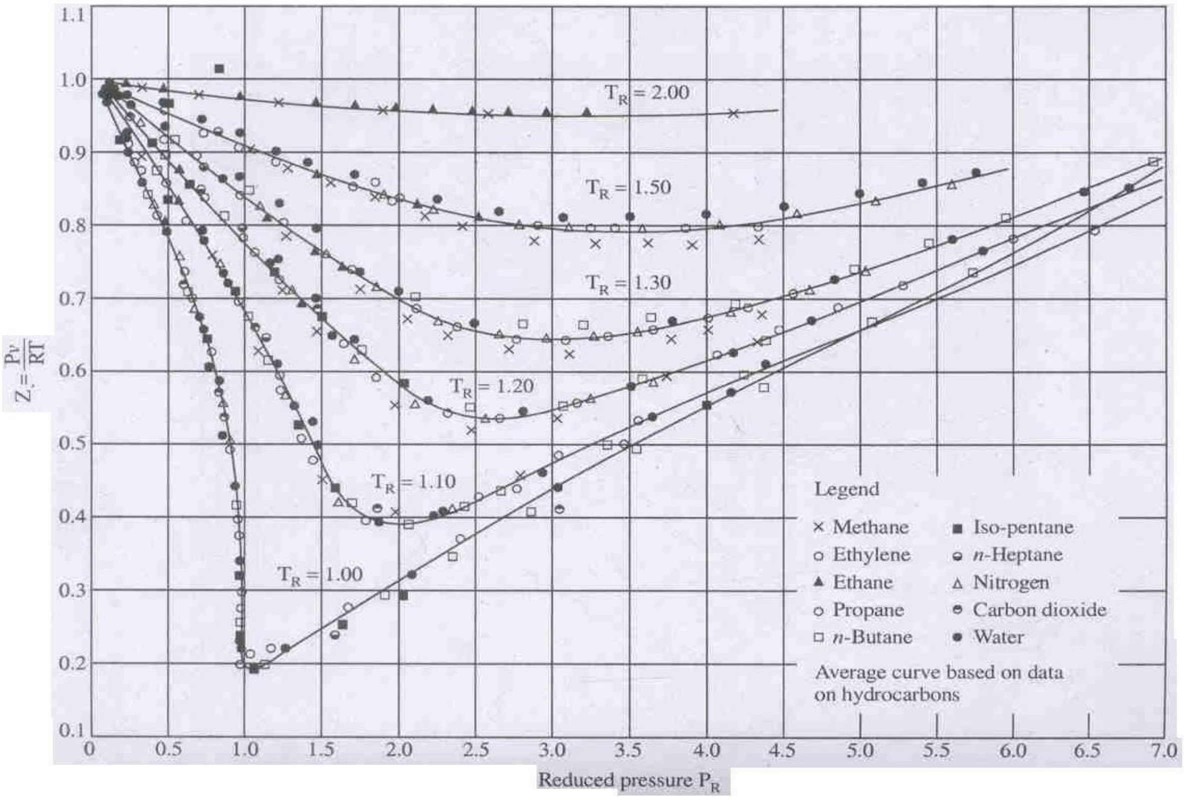
The real gases follow closely the ideal gas equation only at low pressures and high temperatures. The pressures and temperatures depend on the critical pressure and critical temperature of the real gases. For example – 100^0C is a low temperature for most of the gases, but not for air or nitrogen. Air or nitrogen can be treated as ideal gas at this temperature and atmospheric pressure with an error which is <1%. This is because nitrogen is well over its critical temperature of -147^{0}C and away from the saturation region. At this temperature and pressure most of the substances would exist in solid phase. Hence, the pressure and temperature of a substance is high or low relative to its critical pressure or temperature.

Gases behave differently at a given pressure and temperature, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures. The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the reduced properties.

Generalized Compressibility Chart:

The compressibility factor of any gas is a function of only two properties, usually temperature and pressure so that $Z_1 = f(T_R, P_R)$ except near the critical point. This is the basis for the generalized compressibility chart.

The generalized compressibility chart is plotted with Z versus P_R for various values of T_R. This is constructed by plotting the known data of one or more gases and can be used for any gas.



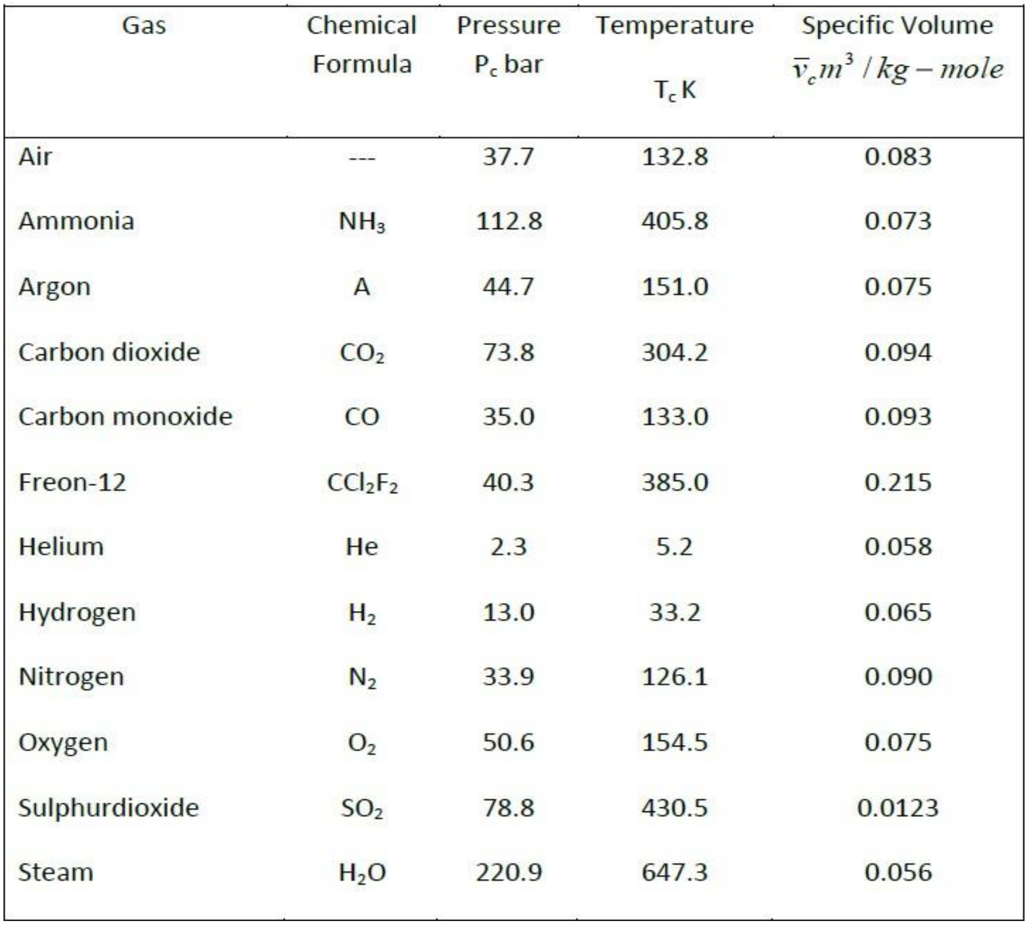
It may be seen from the chart that the value of the compressibility factor at the critical state is about 0.25. Note that the value of Z obtained from Van der waals‟ equation of state at the critical point,

The following observations can be made from the generalized compressibility chart:

- At very low pressures (P_R <<1), the gases behave as an ideal gas regardless of temperature.
- At high temperature (T_R > 2), ideal gas behavior can be assumed with good accuracy regardless of pressure except when (P_R >> 1).
- The deviation of a gas from ideal gas behavior is greatest in the vicinity of the critical point.

The compressibility factor can also be obtained from v-T or v-P data. Since the critical volume may not be consistent with the generalized chart, the pseudo critical specific volume vc1 is used in the definition of reduced volume. It is defined by . The pseudo reduced volume c c c P RT

Table: Critical Point Data of Gases



Gas	Chemical Formula	Pressure P_c bar	Temperature T_c K	Specific Volume $\bar{v}_c m^3 / kg - mole$
Air	---	37.7	132.8	0.083
Ammonia	NH_3	112.8	405.8	0.073
Argon	A	44.7	151.0	0.075
Carbon dioxide	CO_2	73.8	304.2	0.094
Carbon monoxide	CO	35.0	133.0	0.093
Freon-12	CCl_2F_2	40.3	385.0	0.215
Helium	He	2.3	5.2	0.058
Hydrogen	H_2	13.0	33.2	0.065
Nitrogen	N_2	33.9	126.1	0.090
Oxygen	O_2	50.6	154.5	0.075
Sulphurdioxide	SO_2	78.8	430.5	0.0123
Steam	H_2O	220.9	647.3	0.056

Table: Van Der Waals' Constant

Gas	a kN $m^4/(kg\text{-}mol)^2$	b m^3/kg-mol	Z = pv/RT
Air	135.8	0.0365	0.284
Oxygen	138.0	0.0318	0.29
Nitrogen	136.7	0.0386	0.291
Water	551.7	0.0304	0.23
Methane	228.6	0.0427	0.29
Carbon monoxide	147.9	0.0393	0.293
Carbon Dioxide	365.6	0.0428	0.276
Ammonia	424.9	0.0373	0.242
Hydrogen	24.8	0.0266	0.304
Helium	3.42	0.0235	0.30

Problems

1. A rigid vessel of volume 0.3 m3 contains 10 kg of air at 3000K. Using (a) the perfect gas equation, (b) the Vander Walls‟ equation of state and (c) generalized compressibility chart, determine the pressure which would be exerted by the air on the vessel.

Solution: (a) The perfect gas equation is Pv = RT

$$or \quad P = \frac{RT}{v} = \frac{\overline{R}T}{Mv}$$

Specific volume of the gas = $v = \dfrac{0.3}{10} = 0.03 m^3/kg$

From the critical point data of gases, we have T_c = 132.8 K , P_c = 37.7 bar

We can also take the values of a and b from Thermodynamic Data Hand Book. [From table C-8 we have a = 135.8 kN $m^4/(kg\text{-}mol)^2$ and b = 0.0365 m^3/kg-mol]

3. If the values for the reduced pressure and compressibility factor for ethylene are 5 bar and 1.04 respectively, compute the temperature.

Solution: From generated computer chart (from chart 7 in thermodynamic Data Hand Book compiled by B.T. Nijaguna and B.S. Samaga)

We find for $P_R = 5$ & $Z = 1.04$, $T_R = 2.7$

But $T_R = \frac{T}{T_c}$

$\therefore T = (282.4)(2.7)$ Since for ethylene $T_c = 282.4^0K$

$= 762.48^0 K$

4. Using the compressibility chart calculate (a) density of N_2 at 260 bar & 15^0C. (b) What should be the temperature of 1.4 kg of CO_2 gas in a container at a pressure of 200 bar to be have as an ideal gas.

Solution: For N_2. from table C-6 (in thermodynamic Data Hand Book compiled by B.T. Nijaguna and B.S. Samaga) $T_c = 125.9^0K$ $P_c = 3.94$

$$P_R = \frac{P}{P_c} = \frac{260}{33.94} = 7.66, \quad T_R = \frac{T}{T_c} = \frac{288}{125.9} = 2.29$$

$\therefore$ From chart 7, for $P_R = 7.66$ & $T_R = 2.29$, $Z = 1.08$

$$Z = \frac{Pv}{RT} = \frac{P}{\rho RT} \quad i.e., \quad \rho = \frac{P}{ZRT}$$

$$= 281.54 \text{ kg/m}^3$$

(b) For CO_2, from table C–6, $T_c = 304^0K$, $P_c = 73.85$ bar.

As the gas behaves like an ideal gas, Z = 1

$$P_R = \frac{200}{73.85} = 2.71$$

∴ From compressibility chart (chart 7), for Z = 1 & $P_R = 2.71$, $T_R = 2.46$

∴ $T = T_c\, T_R = 304\ (2.46) = 747.84^0K$