



NEHRU COLLEGE OF ENGINEERING AND RESEARCH CENTRE
(NAAC Accredited)
(Approved by AICTE, Affiliated to APJ Abdul Kalam Technological University,
Kerala)



DEPARTMENT OF MECHANICAL ENGINEERING

COURSE MATERIALS



MET202 ENGINEERING THERMODYNAMICS

VISION OF THE INSTITUTION

To mould true citizens who are millennium leaders and catalysts of change through excellence in education.

MISSION OF THE INSTITUTION

NCERC is committed to transform itself into a center of excellence in Learning and Research in Engineering and Frontier Technology and to impart quality education to mould technically competent citizens with moral integrity, social commitment and ethical values.

We intend to facilitate our students to assimilate the latest technological know-how and to imbibe discipline, culture and spiritually, and to mould them in to technological giants, dedicated research scientists and intellectual leaders of the country who can spread the beams of light and happiness among the poor and the underprivileged.

ABOUT DEPARTMENT

- ◆ Established in: 2002

Department of Mechanical Engineering, NCERC Pampady

- ◆ Course offered : B.Tech in Mechanical Engineering
- ◆ Approved by AICTE New Delhi and Accredited by NAAC
- ◆ Affiliated to the University of Dr. A P J Abdul Kalam Technological University.

DEPARTMENT VISION

Producing internationally competitive Mechanical Engineers with social responsibility & sustainable employability through viable strategies as well as competent exposure oriented quality education.

DEPARTMENT MISSION

1. Imparting high impact education by providing conducive teaching learning environment.
2. Fostering effective modes of continuous learning process with moral & ethical values.
3. Enhancing leadership qualities with social commitment, professional attitude, unity, team spirit & communication skill.
4. Introducing the present scenario in research & development through collaborative efforts blended with industry & institution.

PROGRAMME EDUCATIONAL OBJECTIVES

PEO1: Graduates shall have strong practical & technical exposures in the field of Mechanical Engineering & will contribute to the society through innovation & enterprise.

PEO2: Graduates will have the demonstrated ability to analyze, formulate & solve design engineering / thermal engineering / materials & manufacturing / design issues & real life problems.

PEO3: Graduates will be capable of pursuing Mechanical Engineering profession with good communication skills, leadership qualities, team spirit & communication skills.

PEO4: Graduates will sustain an appetite for continuous learning by pursuing higher education & research in the allied areas of technology.

PROGRAM OUTCOMES (POS)

Engineering Graduates will be able to:

1. **Engineering knowledge:** Apply the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of complex engineering problems.
2. **Problem analysis:** Identify, formulate, review research literature, and analyze complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences, and engineering sciences.
3. **Design/development of solutions:** Design solutions for complex engineering problems and design system components or processes that meet the specified needs with appropriate

consideration for the public health and safety, and the cultural, societal, and environmental considerations.

4. **Conduct investigations of complex problems:** Use research-based knowledge and research methods including design of experiments, analysis and interpretation of data, and synthesis of the information to provide valid conclusions.
5. **Modern tool usage:** Create, select, and apply appropriate techniques, resources, and modern engineering and IT tools including prediction and modeling to complex engineering activities with an understanding of the limitations.
6. **The engineer and society:** Apply reasoning informed by the contextual knowledge to assess societal, health, safety, legal and cultural issues and the consequent responsibilities relevant to the professional engineering practice.
7. **Environment and sustainability:** Understand the impact of the professional engineering solutions in societal and environmental contexts, and demonstrate the knowledge of, and need for sustainable development.
8. **Ethics:** Apply ethical principles and commit to professional ethics and responsibilities and norms of the engineering practice.
9. **Individual and teamwork:** Function effectively as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings.
10. **Communication:** Communicate effectively on complex engineering activities with the engineering community and with society at large, such as, being able to comprehend and write effective reports and design documentation, make effective presentations, and give and receive clear instructions.
11. **Project management and finance:** Demonstrate knowledge and understanding of the engineering and management principles and apply these to one's own work, as a member and leader in a team, to manage projects and in multidisciplinary environments.
12. **Life-long learning:** Recognize the need for, and have the preparation and ability to engage in independent and life-long learning in the broadest context of technological change.

PROGRAM SPECIFIC OUTCOMES (PSO)

PSO1: Students will be able to apply principles of engineering, basic sciences & analytics including multi variant calculus & higher order partial differential equations..

PSO2: Students will be able to perform modeling, analyzing, designing & simulating physical systems, components & processes.

PSO3: Students will be able to work professionally on mechanical systems, thermal systems & production systems.

COURSE OUTCOMES

CO1	Understand basic concepts and laws of thermodynamics
CO2	Conduct first law analysis of open and closed systems
CO3	Determine entropy and availability changes associated with different processes
CO4	Understand the application and limitations of different equations of state
CO5	Determine change in properties of pure substances during phase change processes
CO6	Evaluate properties of ideal gas mixtures

MAPPING OF COURSE OUTCOMES WITH PROGRAM OUTCOMES

	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12	PSO1	PSO2	PSO3
CO1	2	2	-	-	-	-	-	-	-	-	-	2	3	2	3
CO2	2	2	1	1	-	-	-	-	-	-	-	1	3	-	3
CO3	3	3	2	2	-	-	-	-	-	-	-	1	3	2	3
CO4	2	2	2	2	-	-	-	-	-	-	-	1	3	2	3
CO5	3	3	2	1	-	-	-	-	-	-	-	1	3		3
CO6	3	3	2	2	-	-	-	-	-	-	-	1	3	2	3

Note: H-Highly correlated=3, M-Medium correlated=2, L-Less correlated=1

SYLLABUS

Module 1: Role of Thermodynamics and its applications in Engineering and Science –Basic Concepts Macroscopic and Microscopic viewpoints, Concept of Continuum, Thermodynamic System and Control Volume, Surrounding, Boundaries, Types of Systems, Universe, Thermodynamic properties, Process, Cycle, Thermodynamic Equilibrium, Quasi – static Process, State, Point and Path function. Zeroth Law of Thermodynamics, Measurement of Temperature, reference Points, Temperature Scales.

Module 2: Energy - Work - Pdv work and other types of work transfer, free expansion work, heat and heat capacity. Joule's Experiment- First law of Thermodynamics - First law applied to Non flow Process- Enthalpy- specific heats- PMM1, First law applied to Flow Process, Mass and Energy balance in simple steady flow process. Applications of SFEE, Transient flow –Filling and Emptying Process, Limitations of the First Law.

Module 3: Second Law of Thermodynamics, Thermal Reservoir, Heat Engine, Heat pump – Kelvin-Planck and Clausius Statements, Equivalence of two statements, Reversibility, Irreversible Process, Causes of Irreversibility, PMM2, Carnot's theorem and its corollaries, Absolute Thermodynamic Temperature scale. Clausius Inequality, Entropy- Entropy changes in various thermodynamic processes, principle of increase of entropy and its applications, Entropy generation, Entropy and Disorder, Reversible adiabatic process- isentropic process, Third law of thermodynamics, Available Energy, Availability and Irreversibility- Second law efficiency.

Module 4: Pure Substances, Phase Transformations, Triple point, properties during change of phase, T-v, p-v and p-T diagram of pure substance, p-v-T surface, Saturation pressure and Temperature, T-h and T-s diagrams, h-s diagrams or Mollier Charts, Dryness Fraction, steam tables. Property calculations using steam tables. The ideal Gas Equation, Characteristic and Universal Gas constants, Deviations from ideal Gas Model: Equation of state of real substances, Vander Waals Equation of State, Virial Expansion, Compressibility factor, Law of corresponding state, Compressibility charts.

Module 5: Mixtures of ideal Gases – Mole Fraction, Mass fraction, Gravimetric and volumetric Analysis, Dalton's Law of partial pressure, Amagat's Laws of additive volumes, Gibbs-Dalton's law Equivalent Gas constant and Molecular Weight, Properties of gas mixtures: Internal Energy, Enthalpy, specific heats and Entropy, Introduction to real gas mixtures- Kay's rule. General Thermodynamic Relations – Combined First and Second law equations – Helmholtz and Gibb's functions - Maxwell's Relations, Tds Equations. The Clapeyron Equation, equations for internal energy, enthalpy and entropy, specific heats, Throttling process, Joule Thomson Coefficient, inversion curve.

QUESTION BANK

MODULE I			
Q:N O:	QUESTIONS	CO	K L
1	Compare (i) statistical & classical thermodynamics (ii) Point & Path function with examples (iii) Intensive & Extensive properties with examples.	CO1	K2
2	Compare Gas thermometer with Thermocouple. Also draw labelled diagrams of both thermometers.	CO1	K3
3	Explain the concept of continuum. Compare (i) reversible and ir-reversible process (ii) Flow and Non- Flow process with examples.	CO1	K2
4	Explain any Four types of work transfer with neat figures.	CO1	K2
5	Differentiate (i)Heat and Work (ii) Open & Closed cycle (iii) Quasi static process and reversible process.	CO1	K2
6	(a) Define (i) Zeroth law of thermodynamics (ii) Specific heat (b) Explain (i) Free expansion work (ii) Paddle work	CO1	K2
7	(a) A gas undergoes a reversible non flow process according to the relation $P = (-2V + 20)$ bar Where V is volume in m^3 and P is the pressure. Calculate the work done when the volume changes from $4 m^3$ to $8m^3$. (b) With neat figure explain resistance thermometer.	CO1	K2
8	(a) Distinguish between change of state, path and process. (b) Explain what you understand by thermodynamic equilibrium. (c) convert the following readings of pressure to kpa, assuming that the barometer reads 769mm of Hg: (a) 90 cmHg gauge (b) 3.1 bar	CO1	K2
9	(a)Give reason why the temperature of triple point of water is now used as the standard fixed point of thermometry. Also explain a fixed point. (b) why gas is chosen as the standard thermometric substance. Also explain thermometric property. (c) Describe Ideal gas temperature scale.	CO1	K2
10	Write short notes on (i) Different forms of energy (ii) system, boundary & surroundings		

MODULE II

1	(a) State First law of thermodynamics and any two of its corollaries. Also wrote its limitation. (b) During a flow process 5kw paddle wheel work is supplied while the internal energy of the system increases in one minute is 200kj. Find the heat transfer when there is no other form of energy transfer.	CO2	K2
2	(a)With neat figure explain Joules experiment also derive the relation between work and heat. (b) Explain specific heat and Latent heat.	CO2	K4
3	(a) Define (i) work (ii) Internal energy (iii) Enthalpy (b) Derive the expression for work, internal energy and enthalpy for iso thermal process.	CO2	K2
4	1.5 kg of certain gas at a pressure of 8 bar and 20°C occupies the volume of 0.5m ³ . It expands adiabatically to a pressure of 0.9 bar and volume 0.73m ³ . Determine the work done during the process, gas constant, ratio of specific heats, values of two specific heats, change in internal energy and change in enthalpy.	CO2	K5
5	Derive steady flow energy equation. Also explain any two application of steady flow energy equation to engineering system.	CO2	K5
6	(a) In a gas turbine installation, the gases enter the turbine at the rate of 5kg/sec with a velocity of 50m/s and enthalpy of 900kj/kg and leave the turbine with 150m/s and enthalpy of 400kj/kg. The loss of heat from the gases to the surroundings is 25kj/kg. Assume $R = 0.285 \text{ kJ/kg K}$ $C_p = 1.004 \text{ KJ/kg K}$ and inlet conditions to be at 100 kpa and 27°C. Determine the diameter of the inlet pipe. (b) What do you mean by PMM 1.	CO2	K3
7	(a) Derive an expression for energy analysis of variable flow process. Also name any two commonly encountered flow process. (b) An insulated rigid tank of 1.5 m ³ of air with a pressure of 5 bar and 100°C discharges air into the atmosphere which 8s at 1 bar through a discharge pipe till its pressure becomes 1 bar. Calculate (i) velocity of air in the discharge pipe (b) Evaluate the work that can be obtained through frictionless turbine using kinetic energy of that air.	CO2	K5
8	0.5 kg of air initially at 25°C is heated reversibly at constant pressure until the volume is doubled and is then heated reversibly at constant volume, until the pressure is doubled. For the total path, find the work transfer and change in entropy. Sketch the processes of air in P-V and T-S diagram.		
9	Write any five application of steady flow energy equation to various engineering system. Also derive the relations using SFEE.		

10	What do you know about (i) PMM 1 (ii) Enthalpy (iii) Transient flow		
MODULE III			
1	a) Compare the COP of heat pump to that of a refrigerator. What is the reason for their difference.(4) b) Explain the internal and external irreversibility with practical examples. (6)	CO3	K3
2	a) Explain the working of a Carnot cycle using P-v and T-s diagrams. State why a Carnot engine can't be realised?(6) b) An inventor claims that he developed a refrigerator for removing a heat of 1440 kJ/min from a temperature of 0°C to 25°C by receiving an external work of 2 kW. Comment on his claim.(4)	CO3	K3
3	a) Establish the equivalence of Kelvin-Planck and Clausius statements. (4) b) A heat pump working on the Carnot cycle takes in heat from a reservoir at 5°C and delivers heat to a reservoir at 60°C. The heat pump is driven by a reversible heat engine which takes in heat from a reservoir at 840°C and rejects heat to a reservoir at 60°C. The reversible heat engine also drives a machine that absorbs 30kW. If the heat pump extracts 17kJ/s from 5°C reservoir. Determine (a) rate of heat supply from the 840°C source and (b) the rate of heat rejection to the 60°C sink. (6)	CO3	K2
4	a) Establish the Inequality of Clausius? (4) b) Two kg of air at 500 kPa, 80°C expands adiabatically in a closed System until its volume is doubled and its temperature becomes equal to that of the surroundings which is at 100 kPa, 5°C. For this process, determine (a) the maximum work, (b) the change in availability and (c) the irreversibility. For air, take $c_v = 0.718 \text{ kJ/Kg K}$, $u = c_v T$ where c_v is constant, and $pV = mRT$ where p is pressure in kPa, V volume in m^3 , m mass in kg, R a constant equal to 0.287 kJ/kg K , and T temperature in K. (6)	CO3	K3
5	a) Give two statements of second law of thermodynamics and prove its equivalence (5) b) State and explain principle of increase of entropy. Discuss its physical significance.(5)	CO3	K5
6	a) State and prove Clausius inequality. (6) b) What is meant by (i) exergy (ii) dead state (iii) availability (4).	CO3	K3
7	a) Explain the two statements of Second law of thermodynamics. Why PMM2 is impossible(5) b) A heat engine operating between two reservoirs at temperatures 600°C and 40°C drives refrigerator operating between reservoirs at temperatures of 40°C and -15°C. The heat transfer to the heat engine is 2500kJ and the net work output of the combined engine and refrigerator plant is 400kJ. The efficiency of the heat engine and COP of the refrigerator are each 40% of the maximum possible values. Estimate the heat transfer to the	CO3	K2

	refrigerant and net heat transfer to the reservoir at 40°C. (5)		
8	a) State and prove Clausius theorem (5) b) Determine the maximum work obtainable by using one finite body at temperature T and a thermal energy reservoir at temperature T ₀ , T>T ₀ (5)	CO3	K5
9	a) State and prove Clausius' theorem (4) b) A fluid undergoes a reversible adiabatic compression from 0.5MPa, 0.2m ³ to 0.05m ³ according to the law, $pv^{1.3} = \text{constant}$. Determine the change in enthalpy, internal energy and entropy, and the heat transfer and work transfer during the process. (6)	CO3	K5
10	a) Establish the Inequality of Clausius? (5) b) Explain entropy principle and its applications? (5)	CO3	K2

MODULE IV

1	a) Explain the term availability function. For a non-flow process. (4) b) In a power station, water enters the boiler at saturated condition and leaves as saturated steam the saturated steam at 200°C by receiving heat from hot gases in a steam boiler. Find the increase in total entropy of the combined system of gas and water and increase in unavailable energy due to irreversible heat transfer. Assume that the gases are cooled from 1000°C to 500°C and all the heat from gases goes to water without any losses. Take: c_{pg} (for gas) = 1.005 kJ/kg K, h_{fg} (latent heat of steam at 200°C) = 1940.7 kJ/kg. (6)	CO4	K2
2	a) Explain the importance of the critical point during the phase change process of a pure substance using a P-v diagram. (4) b) A pressure cooker contains 1.5 kg of saturated steam at 5 bars. Find the quantity of heat that must be removed from the steam so as to reduce the quality steam to 60% dry. What would be the pressure and temperature of the steam at the new state. (6)	CO4	K1
3	Explain mollier chart, P-V, P-T, P-V-T diagrams for pure substances. (7) b) A domestic food freezer maintains a temperature of -150C. The ambient air temperature is 300°C. If heat leaks into the freezer at the continuous rate of 1.75KJ/S what is the least power necessary to pump this heat out continuously? (3)	CO4	K2
4	a) What is energy, dead state and triple point? (4) b) A rigid vessel contains 1 kg of a mixture of saturated water and saturated steam at a pressure of 0.15 MPa. When the mixture is heated, the state passes through the critical point. Determine (i) The volume of the vessel (ii) The mass of liquid and of vapour in the vessel initially (iii) The temperature of the mixture when the pressure has risen to 3 MPa (iv) The heat transfer required to produce the final state. (6)	CO4	K3
5	a) State and prove Carnot's theorem. (5) b) Define dryness fraction. Draw the p-v-T surface of a substance that contracts on	CO4	K1

	freezing.(5)		
6	Derive the expression for availability of flow process. (10)	CO4	K2
7	a) Why second law is called law of degradation? (3) b) Derive the expression for reversible work done by a closed system if it interacts only with the surroundings.(7)	CO4	K3
8	a) Draw the phase equilibrium diagram for a pure substance on h-s plot with relevant constant property lines. (3) b) Steam flows in a pipeline at 1.5MPa. After expanding to 0.1MPa in a throttling calorimeter, the temperature is found to be 120°C. Find the quality of steam in the pipeline. What is the maximum moisture at 1.5MPa that can be determined with this set-up if at least 5°C of superheat is required after throttling for accurate reading? (7)		
9	a)What is the critical state? Draw the phase equilibrium diagram on p-v coordinates for a substance which shrinks in volume on melting. (4) b)Steam initially at 0.3 MPa, 250°C is cooled at constant volume. (a) At what temperature will the steam become saturated vapour? (b) What is quality at 80°C? (c) What is the heat transferred per kg of steam in cooling from 250°C to 80°C? (6)		
10	a) What is exergy, dead state and triple point? (4) b) A rigid vessel contains 1 kg of a mixture of saturated water and saturated steam at a pressure of 0.15 MPa. When the mixture is heated, the state passes through the critical point. Determine (i)The volume of the vessel. (ii)The mass of liquid and of vapour in the vessel initially. (iii)The temperature of the mixture when the pressure has risen to 3 MPa. (iv)The heat transfer required to produce the final state. (6)		

MODULE V

1	What is the minimum amount of work required to separate 1 mole of air at 27°C and 1 atm pressure (assumed composed of 1/5 O and 4/5 N ₂) into oxygen and nitrogen each at 27°C and 1 atm pressure?	CO5	K2
2	A closed adiabatic cylinder of volume 1 m ³ is divided by a partition into 3 two compartments 1 and 2. Compartment 1 has a volume of 0.6 m ³ and contains methane at 0.4 MPa, 40°C, while compartment 2 has a volume of 0.4 m ³ and contains propane at 0.4 MPa, 40°C. The partition is removed and the gases are allowed to mix. (a) When the equilibrium state is reached, find the entropy change of the universe. (b) What are the molecular weight and the specific heat ratio of the mixture? The mixture is now compressed reversibly and adiabatically to 1.2 MPa. Compute (c) the final temperature of the mixture, (d) The work required per unit mass, and (e) The specific entropy change for each gas. Take c_p of methane and propane as 35.72 and 74.56 kJ/kg mol K respectively.	CO5	K4

3	The gravimetric analysis of dry air is approximately: oxygen = 23%, nitrogen = 77%. Calculate: (a) The volumetric analysis, (b) The gas constant, (c) The molecular weight, (d) the respective partial pressures, (e) The specific volume at 1 atm, 15°C, and (f) How much oxygen must be added to 2.3 kg air to produce . A mixture which is 50% oxygen by volume?	CO5	K4 4
4	Two containers p and q with rigid walls contain two different monatomic gases with masses m_p and m_q , gas constants R_p and R_q , and initial temperatures T_p and T_q respectively, are brought in contact with each other and allowed to exchange energy until equilibrium is achieved. Determine: (a) the final temperature of the two gases and (b) the change of entropy due to this energy exchange.	CO5	K2
5	Two curves, one representing a reversible adiabatic process undergone by an ideal gas and the other an isothermal process by the same gas, intersect at the same point on the p-v diagram. Show that the ratio of the slope of the adiabatic curve to the slope of the isothermal curve is equal to γ .	CO5	K3
6	Determine the ratio of work done during a reversible adiabatic process to the work done during an isothermal process for a gas having $\gamma = 1.6$. Both processes have a pressure ratio of 6.	CO5	K2
7	(iii)Derive: $TdS = C_v dT + T \frac{\beta}{k} dV = C_p dT - TV\beta dp = \frac{k C_v dp}{\beta} + \frac{C_p}{\beta V} dV$	CO5	K2
8	Prove that $C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_p^2 \cdot \left(\frac{\partial p}{\partial V} \right)_T$	CO5	K3
9	Explain Joule-Kelvin Effect		
10	Derive Clausius – Clapeyron equation		

APPENDIX 1

CONTENT BEYOND THE SYLLABUS

S:NO	WEB SOURCE REFERENCES
1	Work and Heat https://nptel.ac.in/content/storage2/courses/downloads_new/LectureNotes/112108148/112108148.zip
2	Availability https://nptel.ac.in/content/storage2/courses/112108148/pdf/Problems_and_solutions.pdf

MODULE 1

FUNDAMENTAL CONCEPTS AND DEFINITIONS

OBJECTIVE:

Students will be familiar with

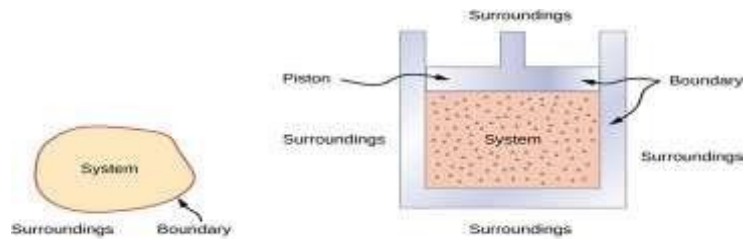
- Thermodynamic concepts.
- Zeroth law of thermodynamics:

Introduction:

- Thermodynamics is derived from two greek words Therme which means HEAT & Dynamics with mean STRENGTH/POWER.
- Thermodynamics is the science of energy transfer and its effect on the physical properties of a substance.
- Its application is in
 - Steam & Nuclear power plant
 - IC Engines
 - Gas turbines
 - Air Conditioning
 - Refrigeration
 - Jet Propulsion Etc.

Basic concepts and definitions:

- **System:** It is defined as a quantity of matter or a Region in space chosen for study.
- **Surroundings/Environment:** The mass or region outside the system is called Surroundings.
- **System Boundary:** The real or imaginary surface that separates the system from its surroundings is called the system boundary or just boundary.
- **Universe:** Combines System & Surroundings forms Universe.



❖ **Types of Systems:**

- a) **Closed system:** System of fixed content or matter (mass) in which only energy transfer takes place is called Closed system. Thus in a closed system, mass doesn't cross the system boundary even though energy may cross the system boundary. For Example of a closed system – a pressure cooker with closed Lid.



Fig 1.1: Closed system

- b) **Open System:** System in which both mass and energy interaction takes place across the system boundary. **For example:** boiling water without a lid. Here Heat escape into the air. At the same time steam (which is matter) also escapes into the air.

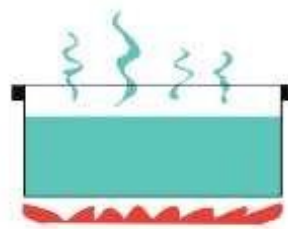
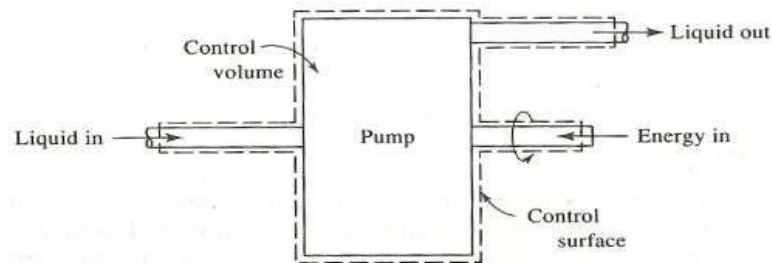


Fig 1.2: Open system

- c) **Isolated System:** In an isolated system neither mass nor energy crosses the system boundary. **For example:** A thermoflask is an isolated system.

- **Control Volume:** It is defined as volume in space through which matter, momentum and energy may flow. The control volume may be stationary or may be moving at a constant velocity. If control volume changes both in size and in position, the control volume is equivalent to an open system. If no mass transfer occurs then it is equivalent to closed system.
- **Control Surface:** Control volume is bounded by a surface called control surface.



Example for Control Volume and Control Surface

- **Macroscopic and Microscopic Approach/Point of View:**

SL.No	Microscopic Approach	Macroscopic approach
1	This approach considers that the system is made up of a very large number of discrete particles known as molecules. These molecules have different velocities and energies.	In this approach the behaviour of individual molecules is not considered but studies the properties of particular mass of the substance.
2	The behaviour of system is found by using statistical method as the number of molecules is very large	The analysis of macroscopic system requires simple mathematical formulae
3	The properties like velocity, momentum, impulse, Kinetic energy etc, which describes the molecules cannot be easily measured by instruments	The properties like temperature and pressure which are required to describe the system can be easily measured by instruments.
4	Large number of variables is needed to describe such a system. So approach is complicated	Only few properties are needed to describe such system

- **Phase:** A Quantity of mater which is homogeneous in chemical composition and in physical structure is called a Phase.

Example: Solid phase: Ice

Liquid Phase: Water

Gaseous Phase: Water vapour /Steam

- **Homogeneous System:** A system is called as Homogeneous system if it consists of a single phase. Example water inside a container.
- **Heterogeneous System:** A system consisting of more than one phase is called Heterogeneous System. Example: Ice in liquid water.
- **Property:** Any characteristic of a system is called Property. It is defined as any quantity that depends on the state of the system and is independent of the path by which the system has reached the given state. Example: Pressure, Volume, Temperature, Mass, Modulus of Elasticity, Electric Resistivity, Thermal Expansion Coefficient Etc.

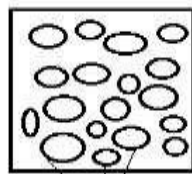
❖ Classification of Property:

- a) **Intensive Property:** Properties that are independent of the mass of the system Example: Temperature, Pressure, Density (**Density of water is constant i.e 1000kg/m³ and the value does not depends on mass of water**).
- b) **Extensive Property:** Properties that are dependent of the mass or extent of the system. Example: Mass, Volume, Entropy, Enthalpy, Energy Etc.
- c) **Specific Property:** Extensive Property Per unit mass are called Specific Property. Example: Specific Volume (v), Specific Enthalpy (h), Specific Energy (e) Etc.

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- **State of a system:** It is the condition of existence of a system at a particular instant. Example: Liquid can exist in Solid liquid & Gaseous phase at each phase the property values will be different which denotes the state of the system.
- **Concept of Continuum:** Since thermodynamics doesn't deal with the behaviour of individual molecule we treat the substance as continuous ignoring the action of individual molecule. This Concept is known as continuum.

“The continuum hypothesis states that large systems made up of many discrete molecules or atoms may be treated as though they are made up of continuous material”

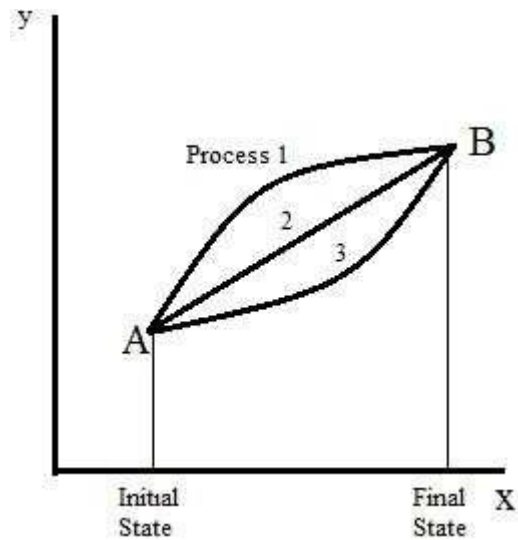


Discrete Molecules

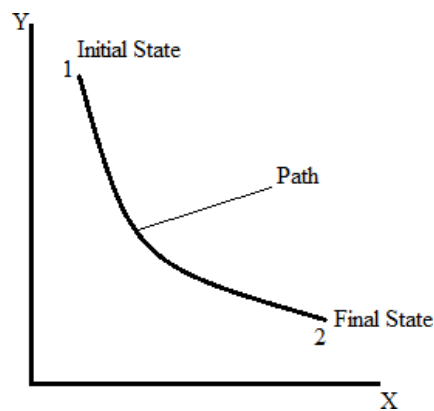


Single Molecule or Continuous material

- **Thermodynamic Process:** It is defined as the path of the thermodynamic states that a system passes through as it goes from an initial state to a final state.



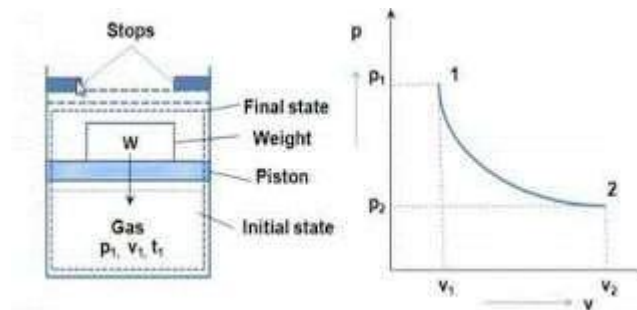
- **Path of a process:** The series of states through which a system passes during a process is called the Path.



- **Equilibrium Process:** If the process goes on so slowly that the state of equilibrium exists at every moment, then such a process is referred to as an equilibrium process otherwise it is referred to as a Non-equilibrium process.
- **Quasi-Static or Quasi-Equilibrium Process:** “When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times is called a Quasi-static Process.

Quasi static process: Example

Let us consider the assembly of cylinder and piston as shown in figure. Cylinder is contained with gas and system is in equilibrium condition initially. Let us see the state of the system initially is at state 1 and indicated by its thermodynamic properties P_1 , V_1 and T_1 . At this state pressure will be high and specific volume will be less at a temperature

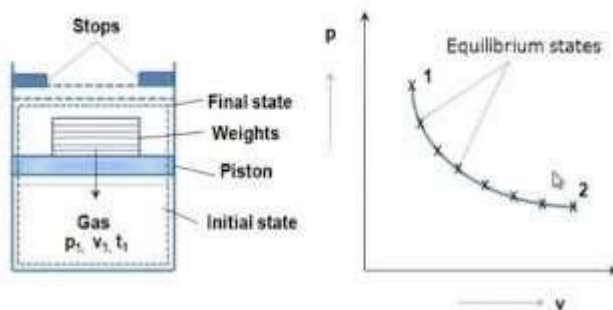


Weight placed over the piston is just balancing the force which is exerted in upward direction by gas. If we remove the weight from the piston, system will have unbalanced force and piston will move in upward direction due to force acting over the piston in upward direction by the gas.

Piston will move in upward direction and will be stopped once it will strike the stops. This condition of the system is expressed as final state and indicated by state 2 and will have its thermodynamic properties P_2 , V_2 and T_2 . At this state pressure will be less and specific volume will be high.

Initial and final state of the system displayed here with the help of thermodynamic properties as state 1 and state 2 respectively, but intermediate states could not be displayed here by thermodynamic properties as intermediate states by which system has arrived at state 2 were not in equilibrium condition.

Quasi-static processes



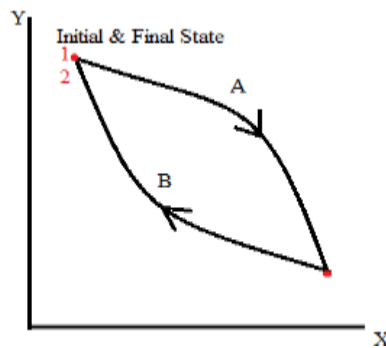
Let us consider the above single weight, placed over the piston, replaced by few infinitesimally small weights and these infinitesimally small weights are placed over each other and also resultant weight of all infinitesimally small weights is equivalent to the single weight placed earlier over the piston.

When we remove the first infinitesimally small weight from the piston, piston will move very slowly as well as with infinitesimally small amount and will secure its next equilibrium state. Due to removal of infinitesimally small weights, one by one and also quite slowly, system will process from one state to another state with succession of equilibrium states.

Hence we can say here that system will arrive to final state from initial state with various equilibrium intermediate states and these intermediate states are displayed in above figure.

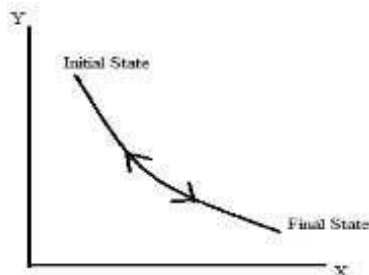
Such a process, where system process in such a manner as studied above, will be termed as quasi static process or quasi equilibrium process in the field of thermal engineering.

- **Thermodynamic Cycle:** It is the one in which a system in a given state goes through a number of different process & finally returns to its initial state .Example: Steam Power Plant constitutes Steam cycle.



From figure the system follows process A and Process B and comes back to initial state 1. If a system undergoes cyclic process then its initial and final state will be same (1 & 2).

- **Reversible Process:** It is defined as the process that occurs in a reverse direction such that the initial state & all energies transferred or transformed during the process can be completely restored in both system and surrounding. In this process there will be no net change in the system or in the surroundings. Example: Reversible adiabatic process.



- **Irreversible Process:** It is defined as the process that is not reversible. Thus during such process the system & the surroundings are no restored to their initial state, if it is restored also their respective

initial states with a net change in the system & in the environment. Example: Flow through pipes involving friction.

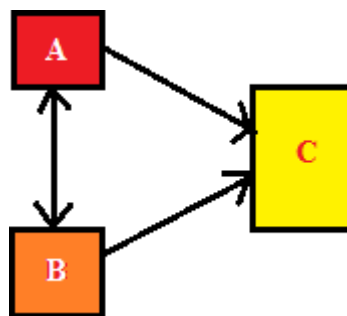
- **Thermodynamic Equilibrium:** When all the conditions of mechanical, chemical, thermal, electrical equilibrium are satisfied, the system is said to be in Thermodynamic Equilibrium.
 1. **Mechanical Equilibrium:** System is said to be in Mechanical equilibrium if there is no unbalanced force within the system or at its boundaries.
 2. **Chemical Equilibrium:** System is said to be in chemical equilibrium when there is no chemical reaction or a process such as diffusion within the system or at its boundaries.
 3. **Thermal Equilibrium:** System is said to be in thermal equilibrium when there is no temperature gradient within the system or between the system and its surroundings.
 4. **Electrical Equilibrium:** System is said to be in electrical equilibrium when there is no electrical potential gradient within a system or between the system and its surroundings.

- **Equality of Temperature:** When two systems at different temperatures are perfectly insulated from the surroundings and brought into contact their will be changes in their physical properties. After some period of time both physical properties and temperature remains constant. This concept is called **Equality of Temperature**.

1.1.1 Zeroth Law of Thermodynamics: “If two bodies are in thermal equilibrium with a third body separately, then they are also in thermal equilibrium with each other.

Or

“If body A is in thermal equilibrium with body B and also separately with body C, then B and C will be in thermal equilibrium with each other.



- **Temperature:** It is the measure of the average heat or thermal energy of the particles in a substance. It does not depend on the size or type of object (**OR**) it is a measure of degree of hotness and coldness of the body.

- **Thermometric property:** The characteristics or physical properties of a reference body which changes with temperature is called thermometric property.
The reference body which is used in the determination of temperature is called **Thermometer**.

Type of thermometer	Thermometric Property	Symbol
Constant Volume Gas Thermometer	Pressure	P
Constant Pressure Gas Thermometer	Volume	V
Electrical Resistance Thermometer	Resistance	R
Thermocouple	Thermal emf	E
Liquid in Glass Thermometer	Length	L

1.1.2 Measurement of temperature:

1) Two standard fixed points method:

To establish a temperature scale an easily reproducible state of an arbitrarily chosen standard system is considered which is called fixed points i.e ICE POINT and STEAM POINT.

ICE POINT: The lower fixed point or ice point is the temperature at which pure ice melts at standard pressure.

STEAM POINT: The upper fixed point or steam point is the temperature at which pure water boils at standard pressure.

These points are considered as fixed points. In this method the thermometer is first placed in contact with the system whose temperature $\theta(X)$ is to be measured, then it is placed in contact with arbitrarily chosen standard system at ice point where temperature is say $\theta(X_1)$. The variation of temperature can be assumed to be a linear function of „X“ which is a thermometric property.

Hence for the first system

$$\frac{\theta(X_1)}{\theta(X)} = \frac{X_1}{X}$$

Then the thermometer at temperature $\theta(X)$ is placed in contact with another chosen standard system at steam point where temperature is $\theta(X_2)$.

Hence for the second system

$$\frac{\theta(X_2)}{\theta(X)} = \frac{X_2}{X}$$

By dividing the equations we get

$$\frac{\theta(X_1) - \theta(X_2)}{\theta(X)} = \frac{X_1 - X_2}{X}$$

$$\theta(X) = \left[\frac{\theta(X_1) - \theta(X_2)}{X_1 - X_2} \right] \cdot X$$

2) Single standard fixed point method:

Kelvin pointed out that a single fixed point such as triple point of water where ice, liquid water and water vapour co-exist in equilibrium. The temperature at which this state exists is arbitrarily assigned the value of 273.16K..If = Triple point of water

X_t = Thermometric property when the body is placed in contact with water at its triple point.

Then we can write,

$$\theta_t = a \cdot X_t$$

$$a = \frac{\theta_t}{X_t} = \frac{273.16}{X_t} \cdot X$$

$$\text{and if } \theta = a \cdot X = \frac{273.16}{X_t} \cdot X$$

$$\theta = \frac{273.16}{X_t} \cdot X$$

Different Types of Thermometer:

- 1) **Liquid in glass thermometer:** A small quantity of liquid enclosed in a glass capillary is called liquid in glass thermometer. In this the thermometer, the expansion of the liquid which is the length of liquid column is used as the thermometric property Example: Mercury in glass

$$\theta(L) \text{ or } T(L) = 273.16 \left[\frac{L}{L_{tp}} \right]$$

thermometer.

- 2) **Constant Volume Gas Thermometer:** It consists of a capillary tube, a gas bulb and a U-tube manometer with flexible tubing. The flexible bend is used to raise or lower the limb which is kept opened to the atmosphere. This helps in adjusting the meniscus of mercury upto the fixed point „A” and hence maintains constant volume in the gas bulb. The capillary tube connects the bulb to one limb of the manometer whereas; the other limb is kept open to atmosphere. The pressure in the bulb is used as a thermometric property and is given by

$$P = P_o + \rho_M \cdot g \cdot h.$$

Where, P_o = Atmospheric pressure, ρ_M = Density of Mercury

When the bulb is brought in contact with the system whose temperature is to be measured, Heat transfer from the system into the bulb takes place and the bulb in course time comes in thermal equilibrium with the system. Due to heat addition the gas in the bulb expands and pushes the mercury level downwards. The flexible limb of the manometer is then adjusted so that the mercury again touches the fixed mark „A” (For keeping volume of gas constant). The difference in the mercury level „h” is recorded and the pressure „P” of the gas in the bulb is estimated by using the formulae. Thus temperature increase is proportional to the pressure increase when volume is kept constant in constant volume gas thermometer.

In **constant pressure gas thermometer** the mercury levels have to be adjusted to keep „h” constant and the volume of gas „V”, which would vary with the temperature of the system becomes the thermometric property. Thus temperature increase is proportional to the volume increase when pressure is kept constant.

International Temperature scale:

Fixed Points	Standard system at 1atm Pressure	Temperature	
		°C	K
Oxygen point	Normal boiling point of oxygen	-182.97	90.19
Ice point	Melting point of ice	0	273.16
Steam point	Normal boiling point of water	100	373.16
Sulphur point	Normal boiling point of sulphur	444.60	717.76
Silver point	Melting point of silver	960.80	1233.96
Gold point	Melting point of gold	1063	1336.16

Different types of scales:

Temperature Scale	Ice point	Steam Point	Triple Point
Kelvin Scale	273.15K	373.15K	273.16K
Rankine Scale	491.67R	671.67R	491.69R
Fahrenheit Scale	32°F	212°F	32.02°F
Centigrade Scale	0°C	100°C	0.01°C

1.1.3 Comparison of Temperature Scales:

Let the Temperature „T” be linear function of thermometric property „L” of the mercury column. Considering the Celsius scale

$$T = a.L + b \dots\dots\dots(1)$$

Where a and b are constants

Applying the above equation for steam point and ice point respectively, we have

$$100 = a. L_S + b$$

$$0 = a. L_I + b$$

Solving the above equation for a and b we get

$$a = 100 / (L_S - L_I)$$

$$b = -100 / (L_S - L_I)$$

Substituting a and b in equation (1) we get

$$T(^{\circ}C) = \left[\frac{L - L_I}{L_S - L_I} \right] \times 100$$

Similarly for Fahrenheit , Rankine and Klevin scale we get

$$T(^{\circ}F) = \left[\frac{L - L_I}{L_S - L_I} \right] \times 180 + 32$$

$$T(R) = \left[\frac{L - L_I}{L_S - L_I} \right] \times 180 + 491.67$$

$$T(K) = \left[\frac{L - L_I}{L_S - L_I} \right] \times 100 + 273.15$$

Relation between scales:

$$T(^{\circ}\text{C}) = \frac{5}{9} [T(^{\circ}\text{F}) - 32]$$

$$T(^{\circ}\text{C}) = \frac{5}{9} [T(R) - 491.67]$$

$$T(^{\circ}\text{C}) = \frac{5}{9} [T(K) - 273.15]$$

$$T(R) = T(^{\circ}\text{F}) + 459.67 = 1.8 \times T(K)$$

IMPORTANT THEORY QUESTIONS:

- 1) Distinguish between i) Microscopic and Macroscopic approaches ii) Intensive and Extensive property iii) Point and Path function iv) Quasistatic and Actual process v) Open and close system vi) Adiabatic wall and diathermic wall.
- 2) Define thermodynamic equilibrium. Explain different conditions that a system should satisfy to attain thermodynamic equilibrium.
- 3) Explain zeroth law of thermodynamics. How this law forms the basis of temperature measurement.
- 4) Name a few measurements (or) quantities that can be conveniently used as thermometric properties in order to quantify the temperature.

PROBLEMS:

- 1) The reading t_A and t_B of two Celsius thermometers A & B agree at the ice point and steam point and are related by the equation $t_A = L + M.t_B + N.t_B^2$. Between these two points L, M, N are constants. When both are immersed in an oil bath, thermometer „A“ indicates 55 and thermometer „B“ indicates 50. Determine the values of L, M, N and also find the reading on „A“ if „B“ reads 25.

Solution: As the two thermometers A and B agree at the ice point and steam point we have

at Ice point : $t_A = 0$, $t_B =$

$$t_A = L + M.t_B + N.t_B^2$$

$$0 = L + 0 + 0$$

$$\mathbf{L = 0}$$

at Steam point: $t_A = 100$, $t_B =$

$$t_A = L + M.t_B + N.t_B^2$$

$$100 = L + M.100 + N.100^2$$

$$\mathbf{M = 1 - 100.N}$$

when „A“ indicates , „B“ indicates hence

$$t_A = L + M.t_B + N.t_B^2$$

$$55 = 50.M + 2500.N$$

$$11 = 10.M + 500.N$$

Substituting for „M“ in the above equation we get

$$\mathbf{N = \frac{1}{5}}$$

From equation $M = 1 - 100.N$

$$\mathbf{M = 6/5}$$

When thermometer „B“ reads , thermometer „A“ reads

$$t_A = L + M.t_B + N.t_B^2$$

$$t_A =$$

Thus when ‘B’ reads , ‘A’ reads

- 1) The e.m.f in a thermocouple with the test junction at on gas thermometer scale and reference junction at ice point is given by $\epsilon = 0.20.t - 5 \times 10^{-4}.t^2$ mV. The millivoltmeter is calibrated at ice and steam points. What will this thermometer read in a place where the gas thermometer reads

Solution: At ice point, when $t = 0$, $\epsilon_I = 0$ mV

$$\text{At steam point , when } t = 100 \text{ , } \epsilon_S = [0.20 \times 100] - [5 \times 10^{-4} \times (100)^2]$$

$$\epsilon_S = 15 \text{ mV}$$

$$\text{At } t = 50 \text{ , } \epsilon = (0.20 \times 50) - [5 \times 10^{-4} \times (100)^2] = 8.75 \text{ mV}$$

For linear scale we have

$$t(^{\circ}\text{C}) = \left[\frac{\epsilon - \epsilon_I}{\epsilon_S - \epsilon_I} \right] \times 100$$

When $\epsilon = 8.75$ m.V

Thus when gas thermometer reads 50 , thermocouple reads

- 3) In 1709, Sir Issac Newton proposed a new temperature scale. On this scale, the temperature was a linear function on Celsius scale. The reading on this at ice point (0°C) and normal human body temperature (37°C) were 0°N and 12°N , respectively. Obtain the relation between the Newton scale and the Celsius scale.

List of Formulae:

$$1. T(^{\circ}\text{C}) = \frac{5}{9}[T(^{\circ}\text{F}) - 32]$$

$$2. T(^{\circ}\text{C}) = \frac{5}{9}[T(\text{R}) - 491.67]$$

$$3. T(^{\circ}\text{C}) = \frac{5}{9}[T(\text{K}) - 273.15]$$

$$4. T(\text{R}) = T(^{\circ}\text{F}) + 459.67 = 1.8 \times T(\text{K})$$

$$5. T(^{\circ}\text{C}) = \left[\frac{L-L_I}{L_S-L_I} \right] \times 100$$

$$6. T(^{\circ}\text{F}) = \left[\frac{L-L_I}{L_S-L_I} \right] \times 180 + 32$$

$$7. T(\text{R}) = \left[\frac{L-L_I}{L_S-L_I} \right] \times 180 + 491.67$$

$$8. T(\text{K}) = \left[\frac{L-L_I}{L_S-L_I} \right] \times 100 + 273.15$$

OUTCOME: Explains thermodynamic systems, properties, Zeroth law of thermodynamics, temperature scales and energy interactions.

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- <http://www.nptel.ac.in/courses/112104113/4#>

WORK & HEAT

OBJECTIVE: Understand various forms of energy including heat transfer and work

STRUCTURE:

1.2.1 Work

1.2.2 Other types of work transfer

1.2.3 Heat

1.2.4 Comparison between work and heat

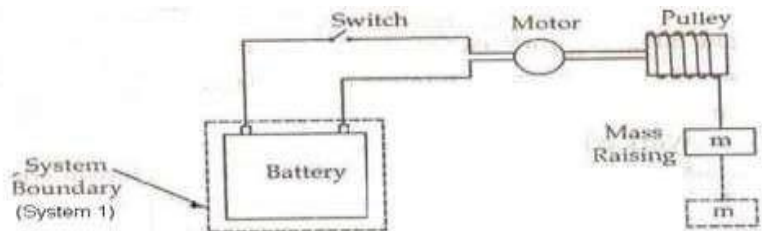
1.2.1 WORK

1. **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, $W = \int$

2. **Thermodynamic definition of work:** Work is the energy transfer across the system boundary in an organized manner such that its sole use could be reduced to lift a weight (mass) against gravitational effect.

Let us consider the battery and the motor as a system. The motor is in turn driving a fan. As the fan rotates, the system (Battery & motor) is doing work upon the surroundings. When fan is replaced by a pulley and a weight, the weight may be raised with the pulley which is driven by the motor. Thus the energy from the system gets transferred to the surrounding in an organized manner and it is utilised to lift the weight against gravitational effect. This energy is called Work.



3. Sign convention for Work:

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



Note: 1) Unit of work is N-m, Joules (J)

- ‖ The rate at which work is done by or upon the system is known as power and its unit is J/s or N-m/s or Watts (W)

4. P.dV work or Displacement Work:

Consider a system which contains a cylinder filled with a gas and a piston moving in the frictionless cylinder as shown in the figure. Let the piston move outward through a small distance „dx” in time interval „dt”. Since the piston moves only a small distance, the pressure acting on the face of the piston can be assumed constant.

The infinitesimal (small amount) workdone by the system is

$$\begin{aligned} &= \text{Force} \times \text{Displacement} \\ &= (P \times \text{Area of the piston} \times \text{Distance moved by the piston}) \\ &= (P \times A \times dx) \\ &= (P \times dV) \quad \{ A \times dx = dV \} \end{aligned}$$

$$= P \times dV$$

If the piston moves through a finite distance, the workdone by the piston is obtained by integrating the above equation between the initial and final state, thus we get

$$\int_1^2 \delta W = \int_1^2 P \times dV = W_{1-2}$$

If the process proceeds from state 2 to state 1 we can write

$$W_{2-1} = \int_2^1 \delta W = \int_2^1 P \times dV$$

This equation is applicable for i) Reversible or frictionless or quasistatic process ii) closed system iii) Effect due to viscous force, magnetic force, gravitational force and electric force are negligible.

5. Point function and Path function:

- ‖ **Point function:** A quantity say „x” that have a value at every point within its domain of definition or a quantity that depends on the states of the system but not on the path followed by the system is called point function. Its derivative is given by „dx” and its integral is

$$\int_1^2 dx = x_2 - x_1$$

Example: All intensive and extensive property

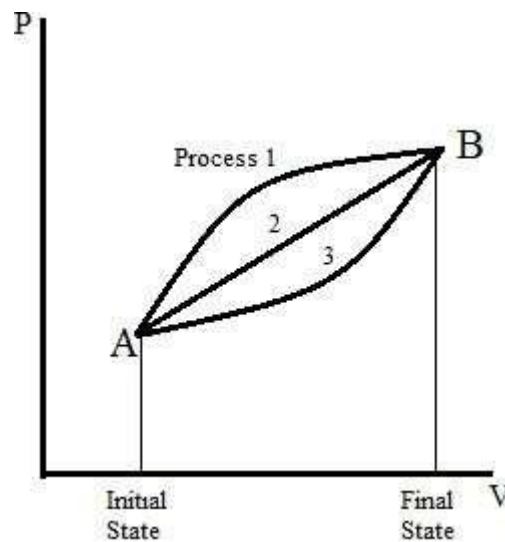
- 2) **Path Function:** A quantity say „y”, whose value depends on the mathematical path followed by the system to reach from initial state to the final state is called path function. It is an exact differential hence its derivative it is denoted by „ δy ”. Thus we can write between two states 1 & 2

$$\int_1^2 \delta y = y_{1-2}$$

6. Prove that work is a path function:

Consider the P-V diagram as shown in the figure. It is possible to reach final state(state 2) from initial state (state 1) or vice versa by following different paths A,B & C. As the area under the curve represents the work for each process, it is evident that the amount of work involved in each process is dependent only on the path followed but not the end points. We can observe that the area under each curve of process is different hence we can conclude that work is a path function. Thus

$$\int_1^2 \delta W = W_{1-2}$$



1.2.2 Other Modes of Work:

- 1) **Shaft Work:** Consider an engine shaft rotated by means of an external force. The shaft undergoes an angular displacement when a constant torque „T” is applied to it
Shaft work is given by

2) **Surface film work or stretching liquid film:**

workdone by the wire frame is given by

$$= \text{Surface tension of a film, } dA = \text{Change in area}$$

for finite changes, \int

3) **Flow work:** work is needed to push the fluid into or out of the boundary of a control volume if mass flow is involved. This work is called the flow work (flow energy). Flow work is necessary for maintaining a continuous flow through a control volume.

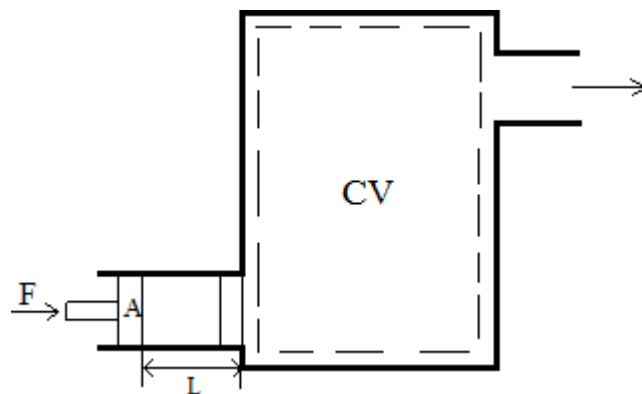
Consider a fluid element of volume V , pressure P , and cross sectional area A as shown in figure. The flow immediately upstream will force this fluid element to enter the control volume, and it can be regarded as an imaginary piston. The force applied on the fluid element by the imaginary piston is $F = P \cdot A$.

The work done due to pushing the entire fluid element across the boundary into the control volume is

$$W_{\text{Flow}} = F \cdot L = P \cdot A \cdot L = P \cdot V$$

$$\text{For unit mass} = w_{\text{flow}} = P \cdot v$$

$$W_{\text{Flow in}} = W_{\text{Flow out}}$$



4) **Stirring Work:**

If „ m “ is the mass of the weight lowered through a distance „ dZ “, then

For finite variation we have,

Special Cases:

1) Restricted or Resisted expansion:

Consider any piston cylinder machine. During expansion of the fluid, the fluid pressure remains uniform throughout the cylinder against a slow moving piston. Such process is called restricted expansion.

The work delivered at the output shaft can be determined by using the equation

—

Where, a = Area of the indicator diagram of Length „ L ”

S = Spring number

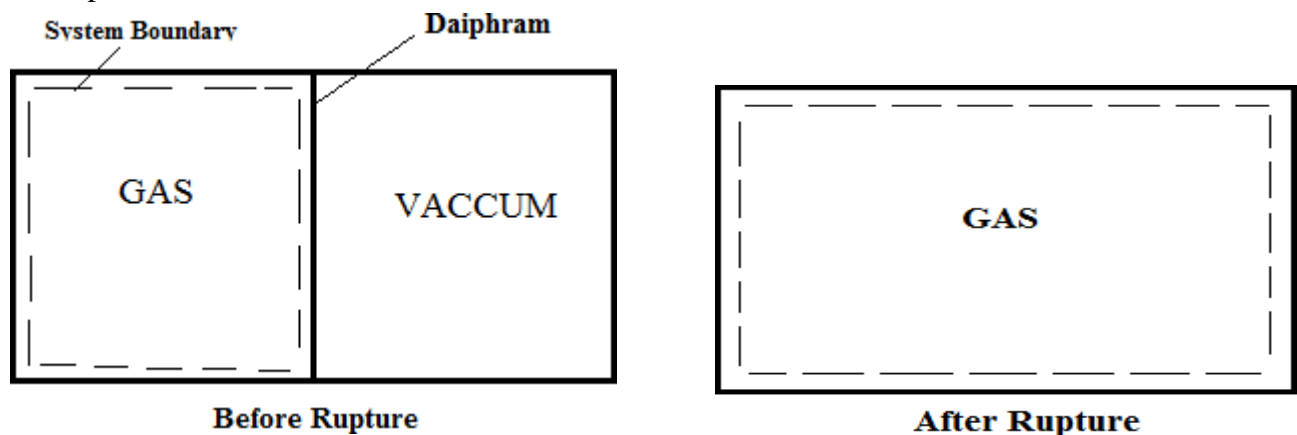
V_s = Swept volume

P_m = Mean effective pressure

If „ N ” is the revolutions per second we have power developed = $P = P_m \cdot L \cdot A \cdot N$

2) Unrestricted Expansion:

Consider a rigid vessel divided by a light diaphragm. One compartment formed by the diaphragm contains a gas whereas the other compartment is evacuated. When the diaphragm is ruptured, the gas moves towards the evacuated compartment. Due to this there will be a change in volume. The process is not reversible even though the initial and final states are in equilibrium. Since vacuum offers no resistance to expansion, the process doesn't pass through equilibrium states and hence there will no well-defined path in turn work transfer will be zero.



1.2.3 HEAT:

Heat is defined as the form of energy that is transferred between two systems or between system and its surroundings by virtue of a temperature difference.

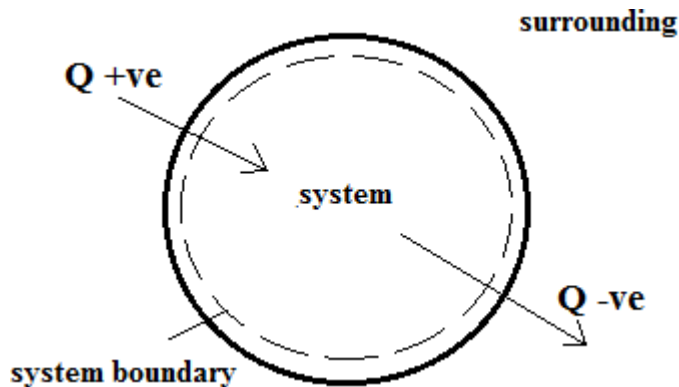
- **Adiabatic process:** A process during which there is no heat transfer is called an adiabatic process ($Q=0$)

Note: Although heat transfer is not there in adiabatic system, The Temperature of a system may change due to work transfer in adiabatic system.

- **Diathermic wall:** A wall which is permeable to heat flow is a diathermic wall.
- **Adiabatic wall:** A wall which is impermeable to heat flow is adiabatic wall.

Sign Convention for Heat:

- Heat transfer into the system is considered as **positive**.
- Heat transfer from the system is considered as **negative**.
- Unit of Heat transfer(Q) is **KJ**



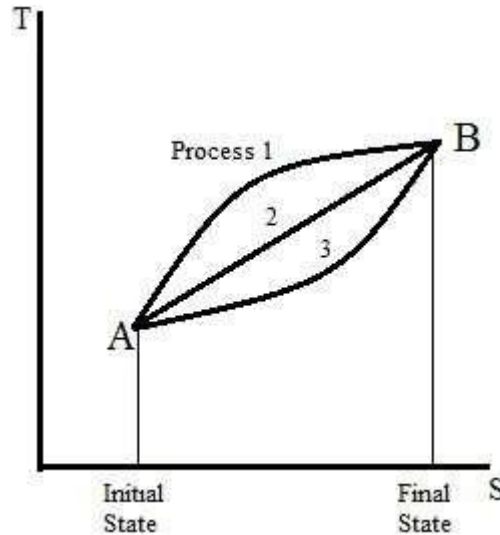
Modes of Heat Transfer:

- 1) **Conduction:** Heat transfer due to direct contact between the elementary particles of a body that is molecules, atoms, free electrons.
- 2) **Convection:** Heat transfer from one body to another by the moving particles of liquid, gas or loose solids during their relative motion in space.
- 3) **Radiation:** Heat transfer by electromagnetic waves through a medium which is transparent to thermal radiation. Fraction of the internal energy of a hot body is converted into radiant energy changing in the form of heat.

Heat is a Path Function:

Similar to work the amount of heat transferred from state 1 to state 2 depends on the path of the system. The area under different process is different hence the amount of heat transfer also varies. Hence for a quasi-static process heat transferred is written as

Where, S = it is an extensive property called Entropy



1.2.4 Comparison between work and heat:

Similarities:

1. Both are path functions and inexact differentials.
2. Both are boundary phenomenon i.e., both are recognized at the boundaries of the system as they cross them.
3. 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.
4. A system possesses energy, but not works or heat.

Dissimilarities:

1. Heat is energy interaction due to temperature difference only; work is by reasons other than temperature difference.
2. In a stable system, there cannot be work transfer; however there is no restriction for the transfer of heat.
3. 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.
4. Heat is a low grade energy whereas work is a high grade energy.

IMPORTANT THEORY QUESTIONS:

1. Define work from thermodynamic point of view and derive an expression for flow work.
2. What are the similarities and dissimilarities between work and heat.
3. Show that work and heat are path function
4. Derive an expression for displacement work or P.dV work for a quasistatic process.
5. Explain briefly a quasistatic process and displacement work.
6. Explain With an example how thermodynamic work is different from mechanics definition of work
7. Specify the most widely used sign convention for work & Heat interaction.
8. Does heat transfer inevitable cause a temperature rise, what is the other cause for rise in temperature.

PROBLEMS:

1. The piston of an oil engine, of area 0.0045m^2 moves downwards 75mm, drawing 0.00028m^3 of fresh air from the atmosphere. The pressure in the cylinder is uniform during the process at 80kPa, while the atmospheric pressure is 101.375 kPa, the difference being due to the flow resistance in the induction pipe and the inlet valve. Estimate the displacement work done by the air.
2. A cylinder contains one Kg of fluid at an initial pressure of 20bar . The fluid is allowed to expand reversibly behind a piston according to law $PV^2 = C$ until the volume is doubled. The fluid is then cooled reversibly with the piston firmly locked in this position until the pressure rises to the original value of 20bar. Calculate the net work done by the fluid for an initial volume of 0.05m^3 .
3. A fluid contained in a horizontal cylinder fitted with a frictionless leak proof piston is continuously agitated by a stirrer passing through the cylinder cover. The diameter of the cylinder is 40cm and the piston is held against the fluid due to atmospheric pressure equal to 100kPa. The stirrer turns 700 revolutions with an average torque of 1Nm. If the piston slowly moves outwards by 50cm determine the net work transfer to the system.
4. A spherical balloon has a diameter of 20cm and contains air at 1.5bar. The diameter of the balloon increases to 30cm in a certain process during which pressure is proportional to the diameter. Calculate the work done by the air inside the balloon during the process.
5. A balloon of flexible material is to be filled with air from a storage bottle until it has a volume 0.7m^3 . The atmospheric pressure is 1.013bar. Determine the work done by the system comprising the air initially in the bottle, given that the balloon is light and requires no stretching.

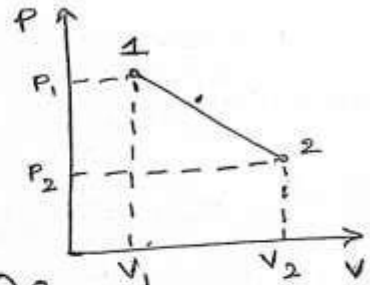
Solution: $\int \int$

$$\begin{aligned} &= \int \{ \text{No change in volume of the bottle hence Zero} \} \\ &= 1 \times (0.7 - 0) \times 100 = 70 \text{ KJ} \end{aligned}$$

Problems :-

→ An engine cylinder has a piston of area 0.12 m^2 & contains gas at a pressure of 1.5 MPa . The gas expands according to a process which is represented by a straight line on p - v diagram. The final pressure is 0.15 MPa . Determine the magnitude & direction of work transfer if the piston stroke is 0.30 m

→ Given A of piston = 0.12 m^2
 $P_1 = 1.5 \text{ MPa}$
 $P_2 = 0.15 \text{ MPa}$
 $L = 0.30 \text{ m}$



$$\begin{aligned} \text{Workdone} &= W_{1-2} = \text{Area under the curve 1-2} \\ &= \frac{1}{2} (V_2 - V_1) (P_1 + P_2) \\ &= (V_2 - V_1) \left[\frac{P_1 + P_2}{2} \right] \end{aligned}$$

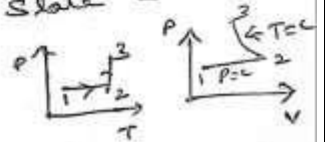
$$W_{1-2} = \frac{1}{2} (P_1 + P_2) (V_2 - V_1) = \frac{1}{2} [1.5 + 0.15] \times 1000 \times (0.12 \times 0.3)$$

$$\boxed{W_{1-2} = 594 \text{ kJ}}$$

+ve hence work is done by the system //

→ An ideal gas contained within a cylinder with a movable piston as shown in fig. Evaluate the work per unit mass by the gas for the path indicated in the system. Assume known conditions at state 1 & 3

$$\begin{aligned} W_{1-3} &= \int_1^3 p \, dv = \int_1^2 p \, dv + \int_2^3 p \, dv \\ &= P_1 (V_2 - V_1) + P_3 V_3 \ln \left(\frac{V_3}{V_2} \right) \end{aligned}$$



$$V_2 = \frac{RT_2}{P_2} = \frac{RT_3}{P_2} = \frac{RT_3}{P_1}$$

3) A spherical balloon of 1m diameter contains a gas at 250 kpa and 300K. The gas inside the balloon is heated until the pressure reaches to 500kpa. During the process of heating, the pressure of gas inside the balloon is proportional to the diameter of the balloon. Calculate the work done by the gas inside the balloon.

→ Given :- $D = 1\text{m}$
 $P_1 = 250\text{kpa}$
 $T_1 = 300\text{K}$
 $P_2 = 500\text{kpa}$
 $P \propto D$
 ${}_1W_2 = ?$

As pressure is proportional to diameter of the balloon

$$P \propto D$$

$$P = C D \text{ where 'C' is a constant} \rightarrow \textcircled{1}$$

Substituting given values in equation ①

$$250 = C \times 1$$

$$\therefore C = 250 \text{ kpa/m}$$

Now $P_2 = C \cdot D_2$

$$500 = 250 \times D_2$$

$$\therefore D_2 = 2\text{m}$$

Volume of the balloon is given by

$$V = \frac{\pi}{6} D^3 \rightarrow \textcircled{2}$$

$$\left\{ V = \frac{4}{3} \pi r^3 \right\} \text{Volume of sphere}$$

Differentiating eqn ② we get

$$dV = \frac{\pi}{6} \times 3D^2 = \frac{\pi}{2} \cdot D^2 dD$$

$$\text{work done} = {}_1W_2 = \int_1^2 P \cdot dV = \int_1^2 C D \times \frac{\pi}{2} D^2 \cdot dD = \int_1^2 \frac{\pi}{2} \cdot C \cdot D^3 \cdot dD$$

$${}_1W_2 = \frac{C\pi}{8} (D_2^4 - D_1^4) = \frac{\pi \times 250}{8} (2^4 - 1^4)$$

$$\boxed{{}_1W_2 = 1472.63 \text{ kJ}}$$

1) Consider the system shown in fig. Initial conditions of the gas are $V_1 = 0.1 \text{ m}^3$ & $P_1 = 200 \text{ kPa}$. The ambient atmosphere pressure is 100 kPa . The spring exerts a force which is proportional to the displacement from its equilibrium position. The gas is heated until the volume is doubled at which point $P_2 = 600 \text{ kPa}$. Determine the work done by the gas.

→ Force balance at any position

Total pressure acting on system = Force due to atmospheric air + Force due to the spring

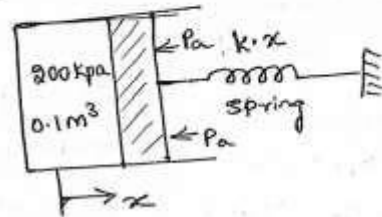
$$p \cdot A = P_a \cdot A + k \cdot x$$

$$\left\{ \because F \propto x \Rightarrow F = k \cdot x \right\}$$

$$\text{Displacement } = x = \frac{\text{Volume}(V)}{\text{Area}(A)}$$

$$\therefore p \cdot A = P_a \cdot A + k \cdot \frac{V}{A}$$

$$\boxed{P = P_a + k \cdot \frac{V}{A^2}} \Rightarrow \textcircled{1}$$



$$\text{Work done is given by } {}_1W_2 = \int_1^2 P \cdot dV = \int_1^2 \left(P_a + k \cdot \frac{V}{A^2} \right) \cdot dV$$

Given

$$\left. \begin{aligned} P_1 &= 200 \text{ kPa} \\ V_1 &= 0.1 \text{ m}^3 \\ P_2 &= 600 \text{ kPa} \\ V_2 &= 2V_1 = 0.2 \text{ m}^3 \end{aligned} \right\}$$

$${}_1W_2 = \int_1^2 P_a \cdot dV + \int_1^2 k \cdot \frac{V}{A^2} \cdot dV$$

$${}_1W_2 = P_a (V_2 - V_1) + \frac{k}{A^2} \times \left[\frac{V_2^2 - V_1^2}{2} \right]$$

$${}_1W_2 = P_a (V_2 - V_1) + \frac{k}{2A^2} [(V_2 + V_1)(V_2 - V_1)]$$

$${}_1W_2 = (V_2 - V_1) \left[P_a + \frac{k}{2A^2} (V_2 + V_1) \right]$$

From equation (1) $k \cdot \frac{V}{A^2} = (P - P_a)$

at state 1 we can write $k \cdot \frac{V_1}{A^2} = P_1 - P_a$

at state 2 we can write $k \cdot \frac{V_2}{A^2} = P_2 - P_a$

$$\therefore {}_1W_2 = (V_2 - V_1) \left[P_a + \frac{P_2 - P_a}{2} + \frac{P_1 - P_a}{2} \right]$$

$${}_1W_2 = (V_2 - V_1) \left[\frac{P_1 + P_2}{2} \right] = (0.2 - 0.1) \left[\frac{200 + 600}{2} \right] = 40 \text{ kJ}$$

5) A piston & cylinder machine containing a fluid system has a stirring device as shown. The piston is frictionless, & it is held down against the fluid due to atmospheric pressure of 101.3 kPa. The stirring device is turned 9500 revolutions with an average torque against the fluid of 1.25 N·m. Meanwhile the piston of 0.65 m diameter moves out 0.6 m. Find the net work transfer of the system.

→ Work done by the stirring device upon the system = shaft work

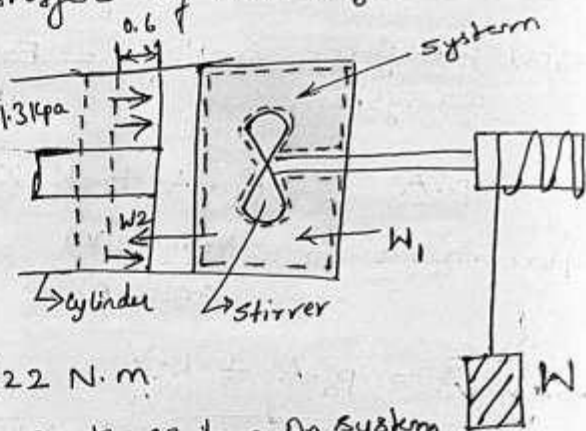
$$T = F \cdot r$$

$$S = 2\pi r \cdot N$$

$$W_{sh} = F \cdot S = 2\pi r \cdot NT = W_1$$

$$W_1 = 2 \cdot \pi \cdot 9500 \cdot 1.25 = 74622 \text{ N}\cdot\text{m}$$

$$W_1 = 74.622 \text{ KJ} \quad \text{negative work } \because \text{ done on system}$$



Work done by the system upon the surroundings

$$W_2 = F \cdot L = p \cdot A \cdot L$$

$$\text{where, } p = 101.3 \text{ kPa, } A = \frac{\pi}{4} \times (0.65)^2 = 0.3318 \text{ m}^2, L = 0.6 \text{ m}$$

$$W_2 = 101.3 \times 0.3318 \times 0.6 = 20.167 \text{ KJ, } +\text{ve work}$$

Hence net work transfer for the system

$$W_{net} = W_1 + W_2 = -74.622 + 20.167$$

$$W_{net} = -54.455 \text{ KJ}$$

A fluid undergoes the following processes in sequence to complete a cycle:

- heated reversibly at $P=c$ of 1.05 bar until it has a volume of 0.02 m^3
- It is then compressed reversibly according to a law $PV=c$ to a pressure of 4.2 bar
- It is then allowed to expand reversibly according to a law $P \cdot 1.3 = c$
- Finally it is heated at constant volume back to initial conditions.

 If the work done during the constant pressure process is $515 \text{ N}\cdot\text{m}$, calculate the net work done on or by the cycle. Sketch the cycle on P - V diagram.

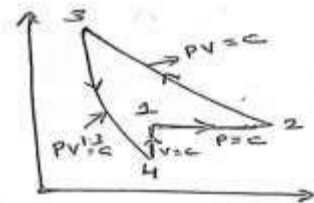
Solution :- Given

$${}_1W_2 = 515 \text{ N}\cdot\text{m}$$

$$P_1 = P_2 = 1.05 \text{ bar} = 1.05 \times 10^5 \text{ Pa}$$

$$P_3 = 4.2 \text{ bar} = 4.2 \times 10^5 \text{ Pa}$$

$$V_2 = 0.02 \text{ m}^3$$



work done during $P=c$ (1-2) process

$${}_1W_2 = P_1(V_2 - V_1) \Rightarrow 515 = 1.05 \times 10^5 (0.02 - V_1)$$

$$V_1 = 0.0151 \text{ m}^3 = V_4$$

To find ${}_2W_3 = P_2 V_2 \ln\left(\frac{V_3}{V_2}\right)$.

$$V_3 = ?$$

To find V_3 , we know that for constant temp process

$$V_3 = \frac{P_2 V_2}{P_3} = \frac{1.05 \times 0.02}{4.2} = 5 \times 10^{-3} \text{ m}^3 //$$

$$\therefore {}_2W_3 = 1.05 \times 10^5 \times 0.02 \ln\left(\frac{5 \times 10^{-3}}{0.02}\right) = -2911.2 \text{ J} //$$

$$\text{To find } {}_3W_4 = \frac{P_3 V_3 - P_4 V_4}{n-1}$$

to find ~~P_4~~ P_4 for an polytropic process

$$\frac{P_3}{P_4} = \left(\frac{V_4}{V_3}\right)^{1.3} \Rightarrow P_4 = 0.998 \text{ bar} //$$

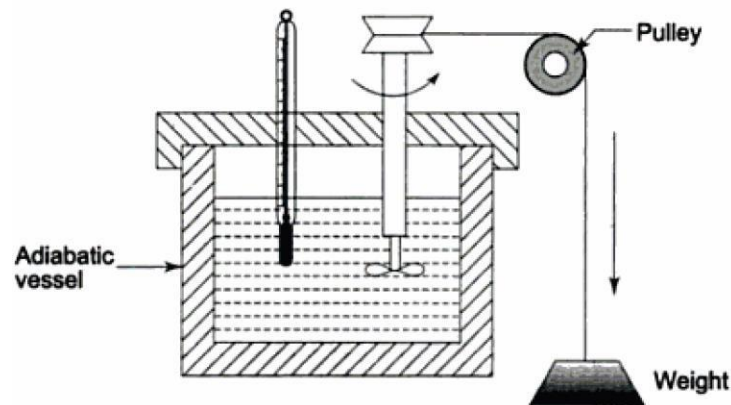
$$\therefore {}_3W_4 = \frac{(4.2 \times 5 \times 10^{-3} - 0.998 \times 0.0151) \times 10^5}{1.3-1} = 1976.7 \text{ J} //$$

$$\text{Net work done} = W_{\text{net}} = {}_1W_2 + {}_2W_3 + {}_3W_4 + {}_4W_1 = -419.5 \text{ J} //$$



MODULE II

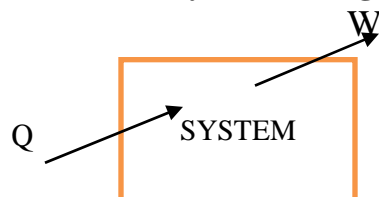
Joule's Experiment



$$\oint dQ = \oint dW$$

- Experimental apparatus consists of insulated cylindrical calorimeter, Spindle consisting of Paddles, Weights, Pulley, String, Thermometer and a Handle.
- A known mass of water M_1 was taken inside the calorimeter
- By rotating the handle the weights were raised through a height „h“, again by rotating the handle in the reverse direction the weights were allowed to fall down through same height „h“.
- The falling weights rotated the spindle and thereby stirring the water contained in the calorimeter as a result mechanical energy was converted into heat & the temperature of the water increased.
- The process was repeated and noted the raise in temperature in each case and found that work transfer is directly proportional to Heat transfer. By conducting a series of experiments Joule found that when the falling weights lost 4.186kJ of Mechanical Energy a temperature of 1kg of water raised by 1°C.
- Thus potential energy of the falling masses was converted into kinetic energy and finally into heat energy

First law applied to closed system undergoing non-cyclic process:



“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.”

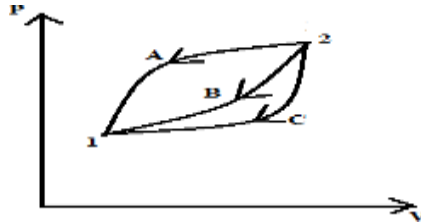
If Q is the amount of heat transferred to the system and W is the work transferred from the system during the process, then,

The Energy in storage is neither heat nor work, but is given the name **internal energy**.

If more than one heat transaction and more than one work transaction are happening at the same time on a system then,

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

Energy a Property of the System:



Existence of property

Modes of Energy:

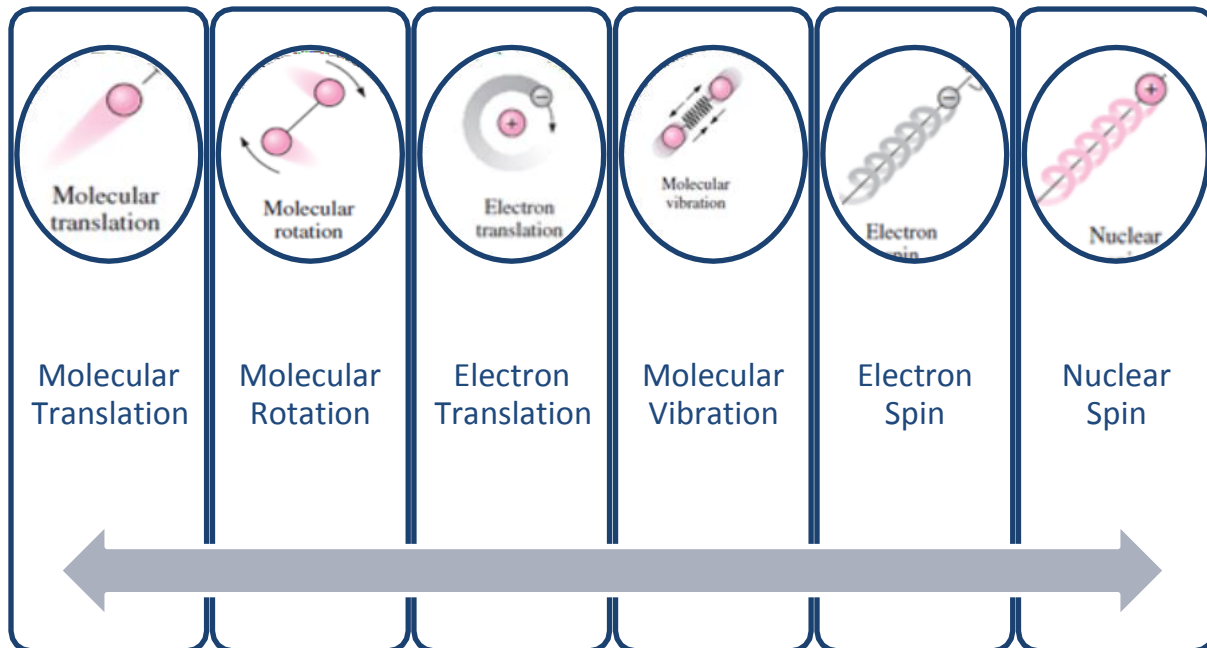
The property E (stored energy) in the first law of TD equation represents the sum of energy transfers across the boundary. This may present in any forms of energy namely, Kinetic energy, Potential energy, Chemical energy, Electrical energy etc.

However, in Thermodynamics it is a practice to consider Kinetic and Potential energies separately and group all other types under one category known as Internal energy (U). Thus,

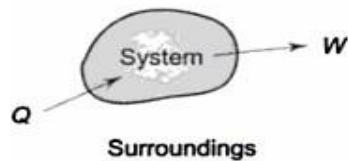
$$E = \text{Internal energy} + \text{Kinetic energy} + \text{Potential energy}$$

In the absence of motion and gravity effect further E reduces to Internal energy only in Thermodynamics.

- Forms of energy
 - Thermal,
 - Mechanical,
 - Kinetic,
 - Potential,
 - Electric,
 - Magnetic,
 - Chemical, and
 - Nuclear,
- Their sum constitutes the total energy E of a system.



- $Q = \Delta E + W$



Energy – A property of the system

Consider a system which changes going from state (1) to state (2) by following the path A and returns to state (1) through path B, such that the system undergoes a thermodynamic cycle.

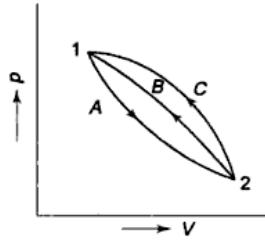


Figure 1 Energy - property of a system

For the process along path A, the first law of thermodynamics can be written as,

$$Q_A = \Delta E_A + W_A$$

Similarly, for path B,

$$Q_B = \Delta E_B + W_B$$

The process along Paths A and B together constitute a cycle, hence the first law can be written for a cycle as

Let the system now repeat the change of state from (1) to (2) along path A, but return to the initial state along path C.

Then,

$$Q_C = \Delta E_C + W_C$$

$$\sum W_{cycle} = \sum Q_{cycle}$$

$$W_A + W_C = Q_A + Q_C$$

$$Q_A - W_A = W_C - Q_C$$

Therefore,

$$\therefore \Delta E_A = -\Delta E_C$$

$$\Delta E_B = \Delta E_C$$

That is, the change in energy between two states of a system is the same, whatever path the system may follow. Therefore, the change in energy is independent of the path followed by the system. Hence it is a point function and a property of the system.

Total Energy, E is an extensive property (Joules).

Specific Energy, $e = \frac{E}{m}$ (J/kg)

PMM1

A hypothetical machine which can produce useful energy(work) without any source or which can produce more energy than consumed. It violates the first law of Thermodynamics.

The macroscopic forms of energy are those a system possesses as a whole with respect to some outside reference frame, such as kinetic and potential energies. The microscopic forms of energy are those related to the molecular structure of a system and the degree of the molecular activity, and they are independent of outside reference frames. The sum of all the microscopic forms of energy is called the internal energy of a system and is denoted by U .

Enthalpy

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

Specific Enthalpy, $h = u + pv$ (Joules/kg)

Enthalpy, $H = U + pV$ (Joules)

Steady Flow Energy Equation

Steady flow process

- 'Steady Flow' means that
 - The rates of flow of mass and energy across the control surface are constant
- At the steady state of a system, any thermodynamic property will have a fixed value at a particular location, and will not alter with time.
- The property might vary along space coordinates, but do not vary with time
Flow rate of fluid entering the system = Flow rate of fluid leaving the system

$$\frac{dm_1}{dt} = \frac{dm_2}{dt}$$

$$w_1 = w_2$$

$$\rho_1 A_1 C_1 = \rho_2 A_2 C_2$$

$$\text{Density} = \frac{1}{\text{specific volume}}$$

$$\rho = \frac{1}{v}$$
$$\therefore \frac{A_1 C_1}{v_1} = \frac{A_2 C_2}{v_2}$$

Energy balance of the steady flow device implies,

Energy entering the system = Energy leaving the system

Energy Entering = Energy of the Fluid + Flow Work + Heat Transfer

$$E_{in} = w_1 e_1 + w_1 p_1 v_1 + \frac{dQ}{dr}$$

Energy of the fluid = internal energy + kinetic energy + potential energy

$$e = u + e_k + e_p = u + \frac{C^2}{2} + gZ$$

Energy Leaving = Energy of the Fluid + Flow Work + Shaft Work Transfer

$$E_{out} = w_2 e_2 + w_2 p_2 v_2 + \frac{dW_x}{dr}$$

$$u_1 + \frac{C_1^2}{2} + gZ_1 + p_1 v_1 + \frac{dQ}{dm} = u_2 + \frac{C_2^2}{2} + gZ_2 + p_2 v_2 + \frac{dW_x}{dm}$$

$$h = u + pv$$

$$\boxed{h_1 + \frac{C_1^2}{2} + gZ_1 + \frac{dQ}{dm} = h_2 + \frac{C_2^2}{2} + gZ_2 + \frac{dW_x}{dm}}$$

This is known as the steady flow energy equation (SFEE)

This can also be written in the form,

$$q - w_x = (h_2 - h_1) + \frac{C_2^2 - C_1^2}{2} + g(Z_2 - Z_1)$$

In the differential form,

$$dq - dw_x = dh + C dC + g dZ$$

Applications of SFEE

The SFEE can be applied to steady flow devices (Open System) like Nozzle, Diffuser, Turbine, Compressor, Throttling Devices, Heat Exchangers etc.

Nozzle and Diffusor

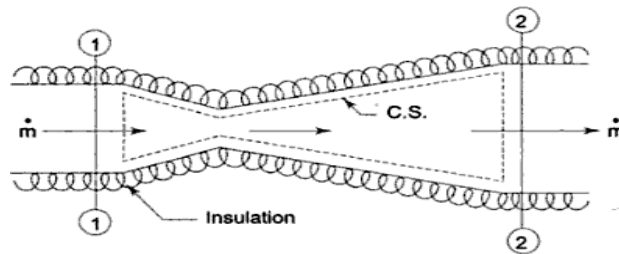


Figure 3 Flow through a nozzle or diffusor

The steady flow energy equation is given by,

$$h_1 + \frac{C_1^2}{2} + \phi_1 + \frac{dQ}{dm} = h_2 + \frac{C_2^2}{2} + \phi_2 + \frac{dW_x}{dm}$$

In a nozzle, $\frac{dQ}{dm} = 0$, $\frac{dW_x}{dm} = 0$, $Z_1 = Z_2$

$$h_1 + \frac{C_1^2}{2} = h_2 + \frac{C_2^2}{2}$$

Where $(h_1 - h_2)$ is in $\left(\frac{\text{kg}}{\text{kg}}\right)$

Flow through a throttling device

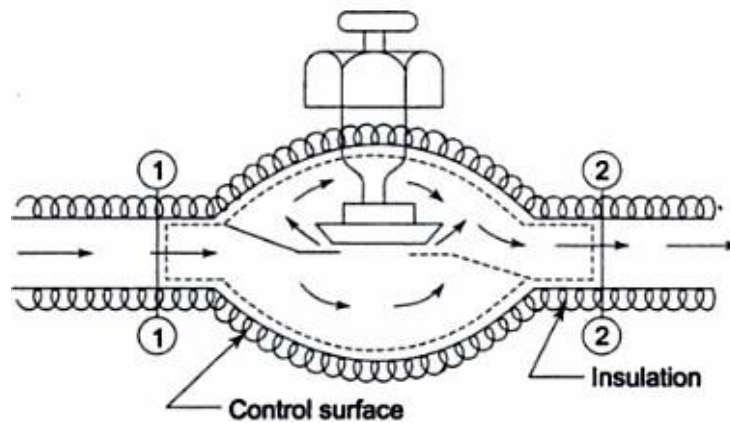


Figure 4 Throttling device or valve

For a valve, $\frac{dQ}{dm} = 0$, $\frac{dW_x}{dm} = 0$, $Z_1 = Z_2$, and K.E. terms are negligible.

Therefore, m

$$h_1 = h_2$$

Flow through a turbine or compress

$$h_1 + \frac{C_1^2}{2} + \mathcal{Z}_1 + \frac{dQ}{dm} = h_2 + \frac{C_2^2}{2} + \mathcal{Z}_2 + \frac{dW_x}{dm}$$

For a turbine, $\frac{dQ}{dm} = 0$, $Z_1 = Z_2$, and K.E. terms are negligible.

$$\frac{dW_x}{dm} = h_1 - h_2$$

For a compressor,

$$\frac{dW_x}{dm} = h_2 - h_1$$

Joule Thompson Effect

Joule–Thomson effect or

Joule–Kelvin effect or

Kelvin–Joule effect or

Joule–Thomson expansion

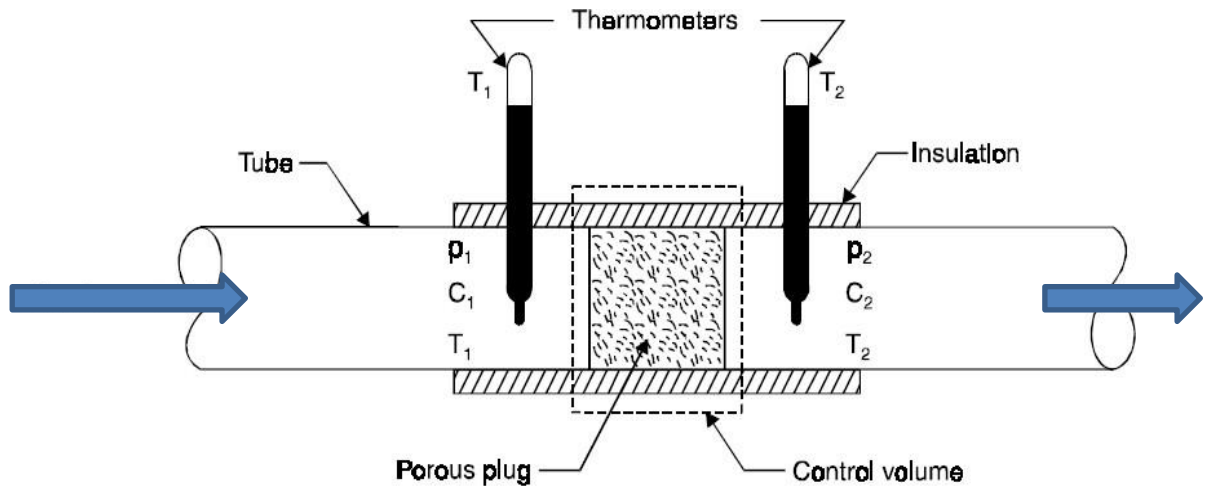
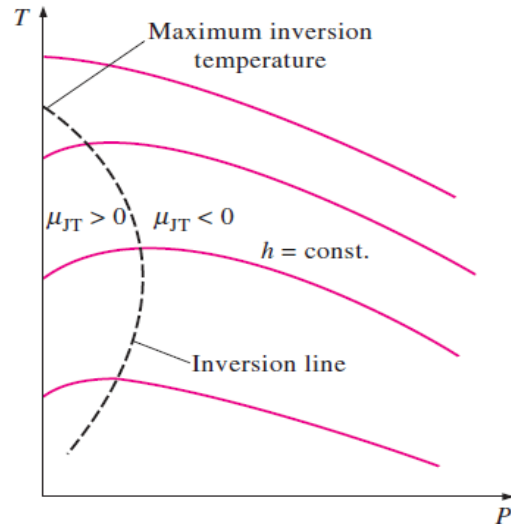


Fig. 4.41. The Joule-Thomson porous plug experiment.

Joule Thompson Coefficient

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

$$\mu_{JT} = \begin{cases} < 0, & \text{Temp. increases} \\ = 0, & \text{Temp. const} \\ > 0, & \text{Temp. decreases} \end{cases}$$



Transient Flow

Many processes involve changes within the control volume with time. Such processes are called unsteady-flow or transient flow processes.

Unlike steady flow processes, transient flow processes start and end over some finite time period instead of continuing indefinitely.

The mass balance for any transient flow system can be expressed as.

$$m_1 - m_2 = m_f - m_i$$

Where,

m_1 = Mass flowing into the system during time period t

m_2 = Mass flowing out of the system during time period t

m_i = Initial Mass of the system

m_f = Final Mass of the system

The energy balance for a transient flow system will give,

$$\text{Total Energy Accumulated} = \text{Energy Inflow} - \text{Energy Outflow}$$

$$E_1 - E_2 = \Delta E_{system}$$

Where,

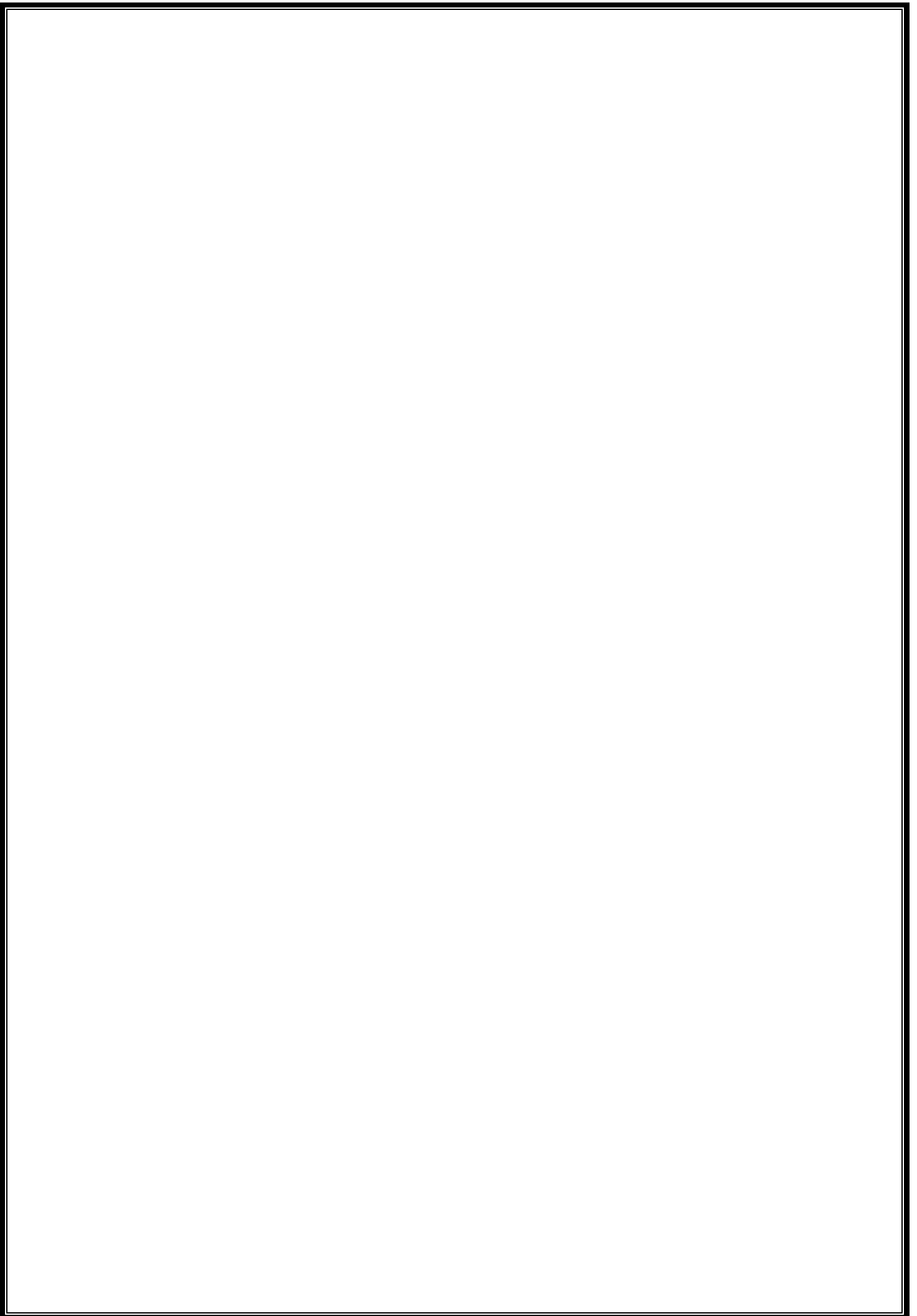
$E_1 - E_2 =$ Net energy transfer by heat, work and mass

$\Delta E_{system} =$ Change in internal, kinetic, potential, etc.. energies.

$$\therefore \Delta E_{system} = m_f e_f - m_i e_i = \{ \Delta Q + m_1 [h_1 + \frac{C_1^2}{2} + Z_1 g] \} - \{ \Delta W_x + m_2 [h_2 + \frac{C_2^2}{2} + Z_2 g] \}$$

Where,

$e_f =$ Final specific energy of the system, $e_i =$ Initial specific energy of the system.



MODULE 3

Second Law of Thermodynamics

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

Heat engine with single thermal reservoir is not possible.

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

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

Thermal Reservoir

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

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

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

Heat Engine

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

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

Thermal Power Plant

Q_2 – Heat rejected to cooling water in condenser

W_P – Work done on the pump

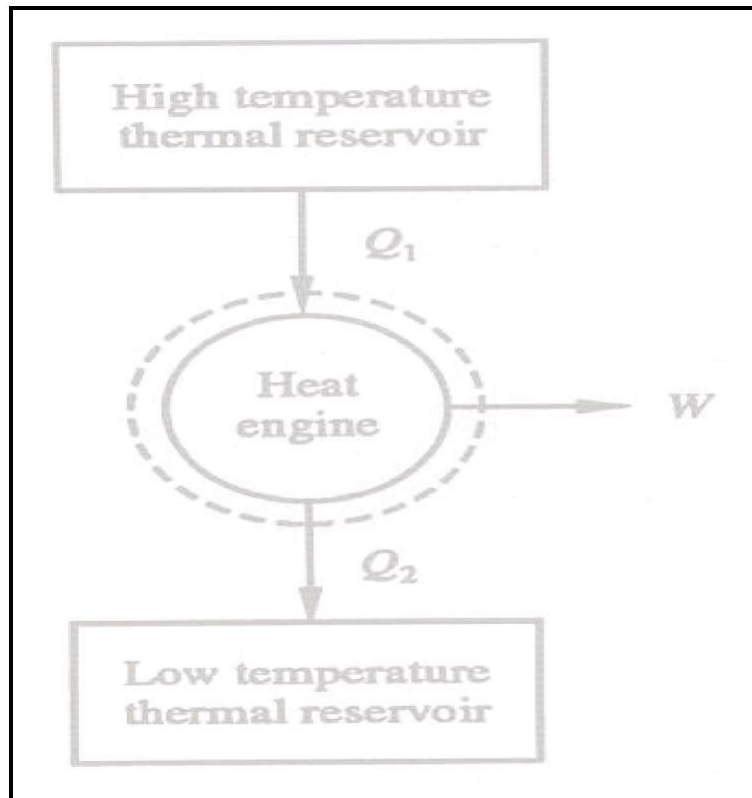
$$W_{\text{net}} = W_T - W_P$$

$$W = Q_1 - Q_2$$

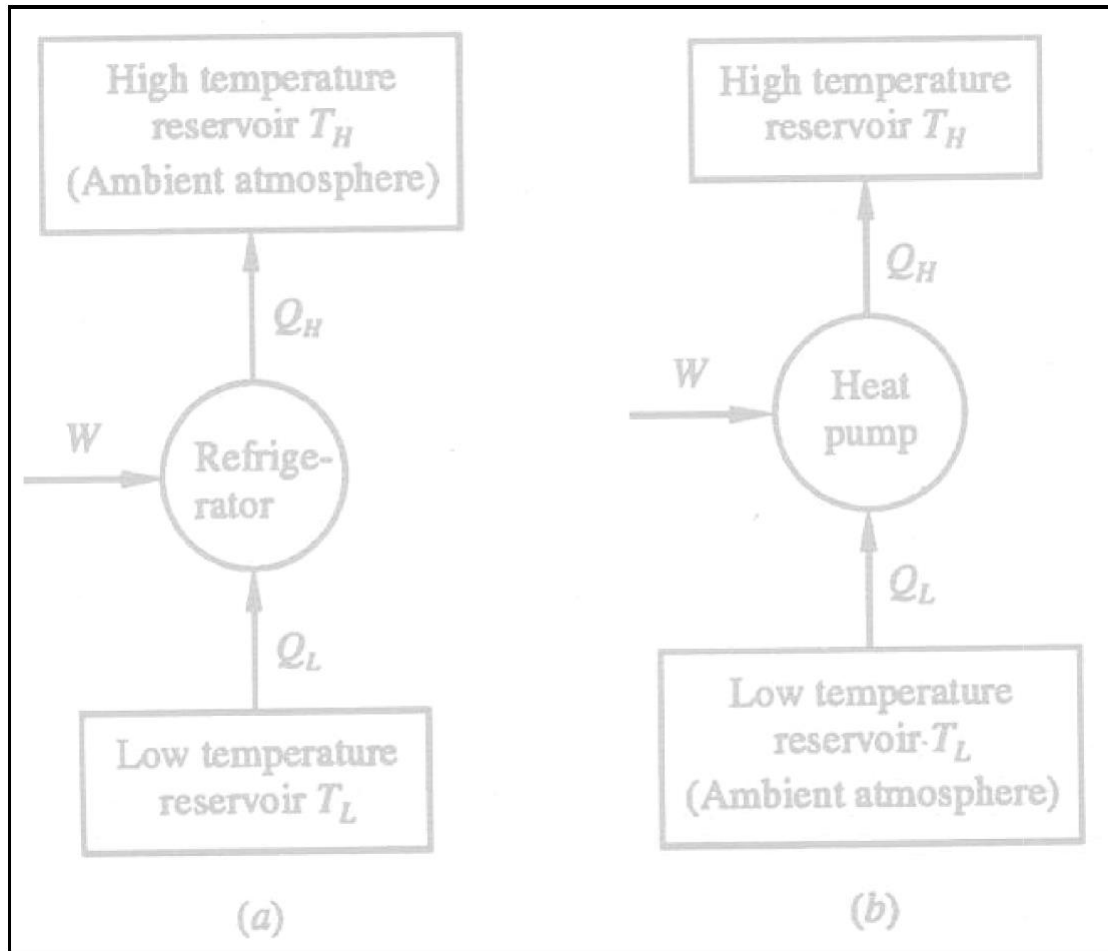
Thermal Efficiency,

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

Schematic representation of Heat Engine:



Schematic representation of Refrigerator and Heat pump.



Q_L – Heat absorbed from low temperature thermal reservoir

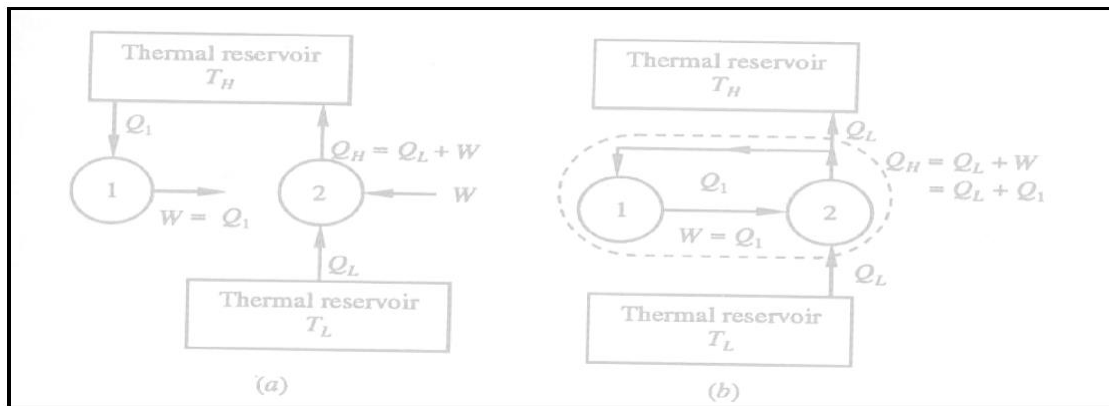
Q_H – Heat rejected to a high temperature thermal reservoir when work (W) is done on it.

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

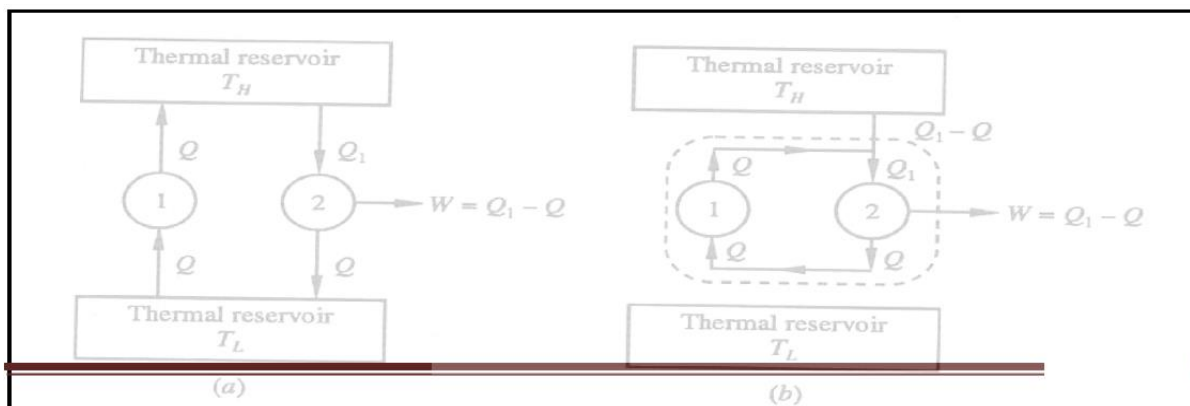
Single reservoir heat engine (1 T engine) is not possible.

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

Equivalence of the two statements



To prove that violation of the Kelvin-Planck Statement leads to a violation of the Clausius



Statement, let us assume that Kelvin-Planck statement is incorrect.

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

Consider another device 2 operating as a cycle, which absorbs energy Q_L as heat from a low temperature thermal reservoir at T_L and rejects energy Q_H ($Q_H=Q_L+W$). Such a device does not violate Clausius statement.

If the two devices are now combined, the combined device (enclosed by the dotted boundary) transfers heat Q_L from the low temperature reservoir at T_L to a high temperature reservoir at T_H without receiving any aid from an external agent, which is the violation of the Clausius statement.

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

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

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

Perpetual Motion Machines

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

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

The first device supplies continuously energy without receiving it. So this is a system creating energy and therefore violating the first law.

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

Reversible and Irreversible Processes

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

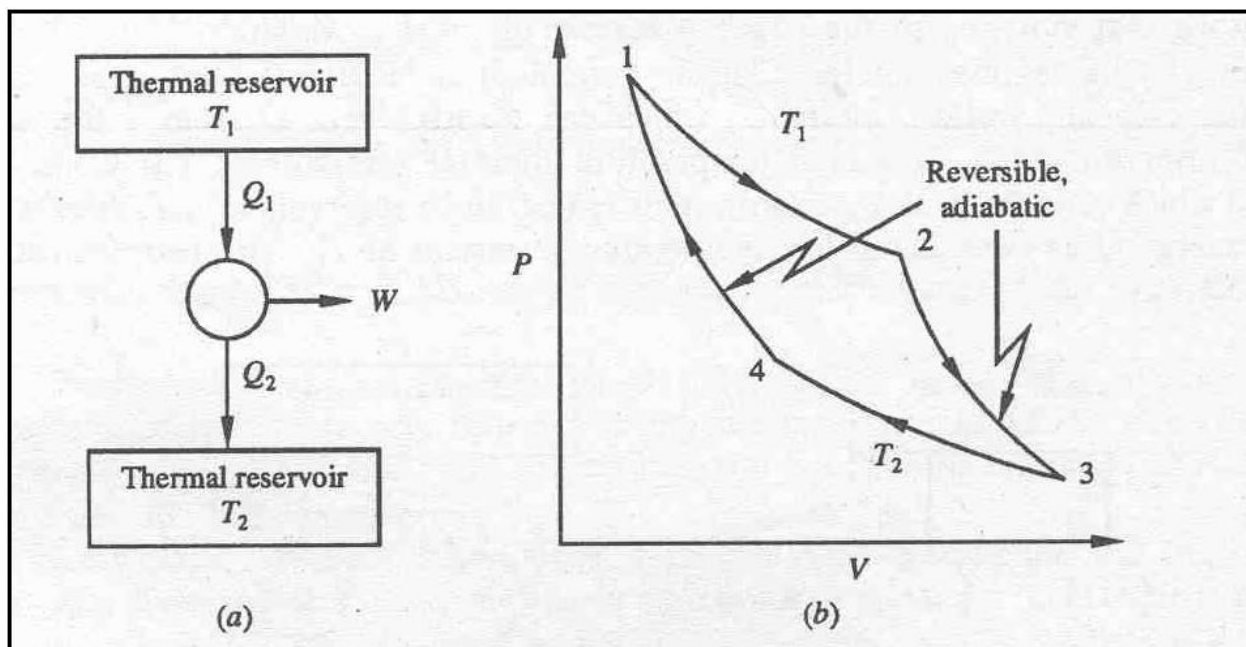
Irreversibilities

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

1. Friction
2. Unrestrained expansion
3. Mixing of two gases
4. Heat transfer across a finite temperature difference
5. Spontaneous chemical reactions

6. Expansion or Compression with finite pressure difference
7. Mixing of matter at different states

Carnot cycle:



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

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

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

The thermal efficiency, η is given by

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

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

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

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

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

$$= 1 - T_2/T_1$$

The Carnot Principles

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

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

$$\eta_I > \eta_R$$

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

$$W_I = Q_1 - Q$$

$$W_R = Q_1 - Q_2$$

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

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

Since $\eta_I > \eta_R$,

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

$$\text{or, } Q < Q_2$$

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

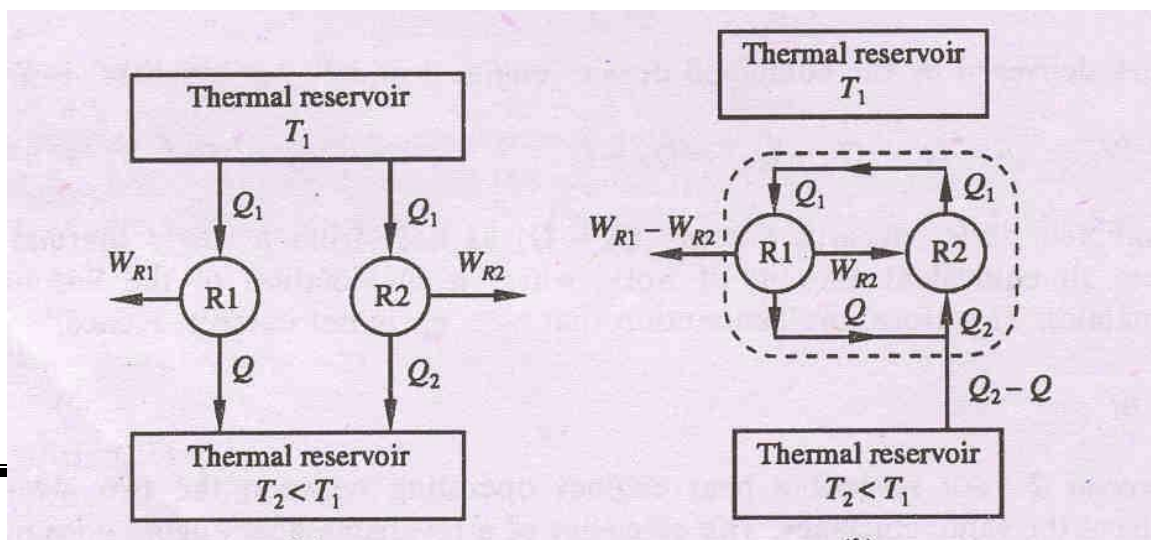
Since the engine R is reversible, it can be made to execute in the reverse order. Then, it will absorb energy Q_2 from the reservoir at T_2 and reject energy Q_1 to the reservoir at T_1 when work W_R is done on it.

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

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

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

Hence, $\eta_R \geq \eta_I$



Carnot principle 2

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

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

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

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

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

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

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

According to assumption,

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

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

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

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

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

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

For the combined device,

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

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

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

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

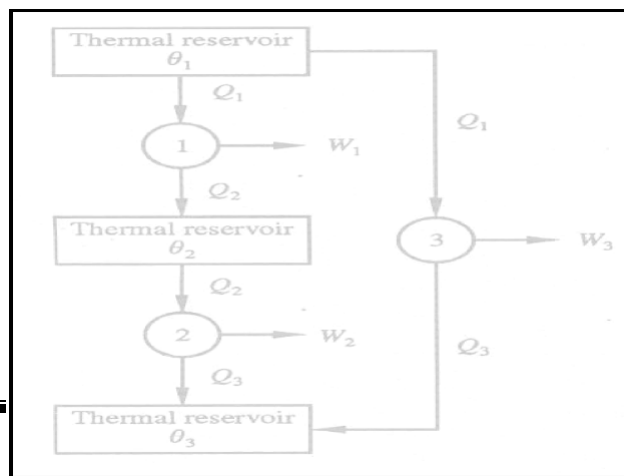
Therefore, based on these two equations,

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

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

Thermodynamic Temperature Scale

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$Q_1/Q_2 = T_1/T_2$$

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

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

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

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

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

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

REVERSIBILITY

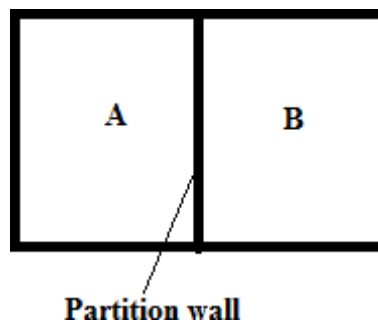
3.1 Reversible process:

A Reversible or ideal process is one in which both the systems and surroundings can be restored to their respective initial states by reversing the direction of process.

3.2 Factors that make process irreversible:

1. Friction
2. Electrical resistance
3. In elastic solid deformation.
4. Free expansion (Unrestrained expansion)
5. Transfer of energy in the form of heat through a finite temperature difference
6. Lack of equilibrium during the process.

3.3 Free expansion process or Unresisted expansion: Consider an adiabatic vessel separated by a partition wall as shown in the figure. If the partition wall is suddenly removed, the air will fill the entire volume of the vessel instantaneously, and this process is not quasi-static and the air is not interacting with surroundings.



To restore original state of the system, the air is to be compressed by an imaginary piston and heat transfer also occurs. These work and heat interactions cause a change in the surroundings and the

surroundings are not restored to their initial states. This indicates that, free expansion is an irreversible process.

3.4 Remarks on carnot Engine:

1. The efficiency of carnot engine depends only on source and sink temperatures and sink temperature and is independent of working fluid. The efficiency becomes maximum when sink temperature $T_2 = 0$, but this is impossible and it violates Kelvin Planck statement of second law.
2. As the temperature difference between source and sink increases, efficiency also increases and is directly proportional to $T_1 - T_2$.
3. The efficiency can be increased either by increasing source temperature or by decreasing sink temperature.

The Carnot Engine is a hypothetical device because:

1. All 4 processes are reversible. For this to happen there should not be any internal friction between particles of working fluid and no friction exists between the piston and cylinder walls.
2. The heat absorption and rejection have to take place with infinitesimal temperature differences.
3. The piston has to move very slowly to achieve isothermal compression or expansion. In the meantime, piston movement must be very fast to achieve adiabatic compression or expansion . It is impossible to achieve different speeds of the piston during different processes.

3.5 Externally Reversible Processes

- No irreversibilities exist in the surroundings.
- Heat transfer can occur between the system and the surroundings, but only with an infinitesimal temperature difference.
- There may be irreversibilities within the system.

3.6 Internally Reversible Processes

- No irreversibilities exist within the system.
- The system moves slowly and without friction through a series of equilibrium states.
- Irreversibilities may exist in the surroundings, usually due to heat transfer through a finite temperature difference.

3.7 CARNOT THEOREM

Define Carnot Theorem and also give its proof.

Carnot theorem states that no heat engine working in a cycle between two constant temperature reservoirs can be more efficient than a reversible engine working between the same reservoirs. In other words it means that all the engines operating between a given constant temperature source and a given constant temperature sink, none, has a higher efficiency than a reversible engine.

Proof:

Suppose there are two engines E_A and E_B operating between the given source at temperature T_1 and the given sink at temperature T_2 .

Let E_A be any irreversible heat engine and E_B be any reversible heat engine. We have to prove that efficiency of heat engine E_B is more than that of heat engine E_A .

Suppose both the heat engines receive same quantity of heat Q from the source at temperature T_1 . Let W_A and W_B be the work output from the engines and their corresponding heat rejections be $(Q - W_A)$ and $(Q - W_B)$ respectively.

Assume that the efficiency of the irreversible engine be more than the reversible engine i.e. $\eta_A > \eta_B$. Hence,

$$W_A/Q > W_B/Q$$

$$\text{I.e. } W_A > W_B$$

Now let us couple both the engines and E_B is reversed which will act as a heat pump. It receives $(Q - W_B)$ from sink and W_A from irreversible engine E_A and pumps heat Q to the source at temperature T_1 . The net result is that heat $(W_A - W_B)$ is taken from sink and equal amount of work is produce. This violates second law of thermodynamics. Hence the assumption we made that irreversible engine having higher efficiency than the reversible engine is wrong.

Hence it is concluded that reversible engine working between same temperature limits is more efficient than irreversible engine thereby proving Carnot's theorem.

Thermodynamic Temperature scale:

A temperature scale which is independent of the property of thermometric substance is known as Thermodynamic temperature scale.

IMPORTANT THEORY QUESTIONS:

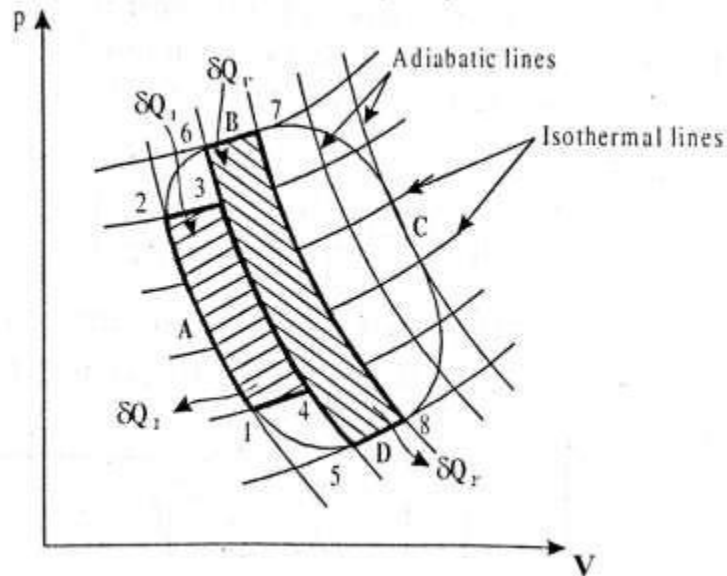
1. List the factors that renders a system reversible.
2. What is thermodynamic temperature scale and deduce the relation between Q and T as proposed by Lord Kelvin.
3. Why it is impossible to carry out the Carnot cycle in real engines.

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- <http://www.nptel.ac.in/courses/112104113/4#>

Entropy: The measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.

Clausius theorem:



- Consider a system undergoing a cycle A-B-C-D as shown in the figure in the p-V diagram.
- This cycle is broken into a large number of small Carnot cycles by a family of reversible adiabatic and reversible isothermal lines on the p-V diagram.
- Thus the whole cycle is represented by a small number of Carnot cycles 1-2-3-4, 5-6-7-8 etc.
- Now consider Carnot cycles 1-2-3-4 and 5-6-7-8. In these two cycles 3-4 and 5-6 represent adiabatic expansion and adiabatic compression respectively in which heat rejection and heat addition takes place. Thus process 3-4 is cancelled out as far as energy transfer with process 5-6 is concerned.
- Also the adiabatics have no contribution to the heat added. Further, if the number of Carnot cycles is very large and the adiabatic lines are close to one another, in the limiting case all these small Carnot cycles coincide with the given reversible cycle A-B-C-D.
- Let Q_1, Q_1', \dots be the amount of heat exchanged during heat absorption and let Q_2, Q_2', \dots be the amount of heat exchanged during rejection.
- Then for small Carnot cycle 1-2-3-4 we may write

we know that for a reversible process $\oint \frac{\delta Q}{T} = 0$

Then we can write $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0 \dots\dots 1$

Similarly for cycle 5-6-7-8

$$\frac{\delta Q_{1'}}{T_{1'}} + \frac{\delta Q_{2'}}{T_{2'}} = 0 \dots\dots 2$$

Adding the equation 1 and 2 we get

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} + \frac{\delta Q_{1'}}{T_{1'}} + \frac{\delta Q_{2'}}{T_{2'}} = \sum \frac{\delta Q}{T} = 0$$

Replacing the summation by cyclic integral in the limit we can write

$$\oint \frac{\delta Q_{rev}}{T} = 0 \text{ ---}$$

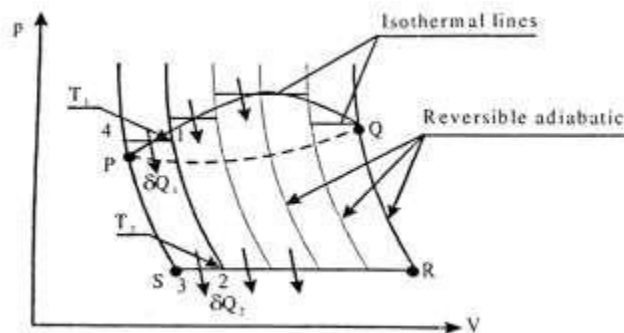
The above equation is known as **CLAUSIUS THEOREM**, Which states that the cyclic integral of $\frac{\delta Q}{T}$ for a **Reversible cycle** is equal to zero

Clausius Inequality:

Consider a cycle PQRS in which process PQ is either reversible or irreversible, whereas other processes QR, RS and SP are reversible as shown in the fig.

Dividing this cycle into large number of smaller cycles and considering any one of such cycles say 1-2-S-4-1, we can write thermal efficiency as

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$



If the cyclic integration is applied to cyclic irreversibilities, then $\oint \frac{\delta Q}{T}$ never becomes Zero.

Thus for any small Carnot cycles operating between temperature T_1 and T_2 with heat exchange δQ_1 and δQ_2 and with some irreversibility the efficiency is smaller than or equal to that of a reversible engine

Thus, $\eta_{irr} \leq \eta_{rev}$

Thus, $\eta_{irr} \leq \eta_{rev}$

$$\text{i.e. } 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_{irr} \leq 1 - \left(\frac{\delta Q_2}{\delta Q_1}\right)_{rev}$$

$$\text{or } \frac{\delta Q_2}{\delta Q_1} \geq \left(\frac{\delta Q_2}{\delta Q_1}\right)_{rev}$$

$$\frac{\delta Q_1}{\delta Q_2} \leq \left(\frac{\delta Q_1}{\delta Q_2}\right)_{rev}$$

But $\left(\frac{\delta Q_1}{\delta Q_2}\right)_{rev} \leq \frac{T_1}{T_2}$

Substituting 2 in 1 we get

$$\frac{\delta Q_1}{\delta Q_2} \leq \frac{T_1}{T_2}$$

In general, if δQ is the heat supplied at temperature 1, then we can modify equation 3 as

$$\frac{\delta Q}{\delta Q_2} \leq \frac{T}{T_2}$$

or

$$\frac{\delta Q}{T} \leq \frac{\delta Q_2}{T_2} \text{ For any process PQ reversible or irreversible}$$

For reversible process,

$$\frac{\delta Q_{rev}}{T} = \frac{\delta Q_2}{T_2}$$

For any process PQ, $\frac{\delta Q}{T} \leq ds$

Thus for any engine working in a cycle

$$\oint \frac{\delta Q}{T} \leq \oint ds$$

THIS IS CLAUSIUS INEQUALITY

Note: If,

$\oint \frac{\delta Q}{T} = 0$, The cycle is reversible

$\oint \frac{\delta Q}{T} < 0$, The cycle is irreversible and possible

$\oint \frac{\delta Q}{T} > 0$ The cycle is impossible since it violates second law.

3.2.9 Entropy is a property:

Consider two reversible paths A and B joining the states 1 and 2.

If path B is reverse, that is transversed from 2 to 1 , then path A and B constitute a reversible cycle.

That is

$$\oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T}_{\text{path A}} + \int_2^1 \frac{\delta Q}{T}_{\text{path B}} \quad \text{---}$$

$$\int_2^1 \frac{\delta Q}{T}_{\text{path B}} = \int_1^2 \frac{\delta Q}{T}_{\text{path A}}$$

It applies to any reversible processes joining states 1 and 2

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

Thus entropy is independent of path and therefore entropy is a property

OUTCOME:

- Explains the concept entropy and its characteristics

IMPORTANT QUESTIONS:

1. State and prove clausius inequality? What is the significance of clausius inequality
2. An adiabatic vessel contains 85kg of oil at a temperature of 27°C. A spherical ball made of steel of 10kg AT 727°C is immersed in oil. Determine change in entropy for the universe. The specific heat of oil = 3.5 kJ/kg.K, Specific heat of steel ball = 0.5kJ/kg.K
3. 0.5 Kg of air initially at 27C is heated reversibly at constant pressure until the volume is doubled and is then heated reversibly at constant volume until the pressure is doubled . For the total path , find work transfer , heat transfer and change of entropy.
4. Explain principle of increase of entropy.
5. Prove that for a cyclic process $\oint \frac{\delta Q}{T} = 0$ Hence define entropy

There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts: Available part, Unavailable part

Available energy: is the maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state (a state in equilibrium with the earth and its atmosphere). Because there can be only one value for maximum work which the system alone could do while descending to its dead state, it follows immediately that „Available energy“ is a property.

Unavailable energy: A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is

4.1. Available energy referred to a cycle:

The available energy (A.E.) or the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 6.1). The minimum energy that has to be rejected to the sink by the second law is called the unavailable energy (U.E.), or the unavailable part of the energy supplied.

$$Q_1 = A.E. + U.E.$$

$$\text{or } W_{\max} = A.E. = Q_1 - U.E.$$

For the given values of the source temperature T_1 and sink temperature T_2 , the reversible efficiency, For a given T_1 , η_{rev} will increase with the decrease of T_2 . The lowest practicable temperature of heat rejection is the temperature of the surroundings, T_0 .

And

Consider a finite process l-m, in which heat is supplied reversibly to a heat engine (Fig. 6.2). Taking an elementary cycle, if dQ_1 is the heat received by the engine reversibly at T_1 ,

Then

$$W_{\max} = A.E. = Q_{l-m} - T_0 (S_1 - S_m)$$

$$\text{or unavailable energy, } U.E. = Q_1 - m - W_{\max}$$

$$\text{or } U.E. = T_0 (S_1 - S_m)$$

Thus unavailable energy is the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat

4.2. Decrease in available energy when heat is transferred through a finite temperature difference:

When transfer of heat takes place through a finite temperature difference, there is a decrease in the availability of energy so transferred. Consider a reversible heat engine operating between temperatures T_1 and T_0

$$Q_1 = T_1 \Delta s$$

$$Q_2 = T_0 \Delta s$$

$$\text{and } W = A.E. = [T_1 - T_0] \Delta s$$

Assume that heat Q_1 is transferred through a finite temperature difference from the reservoir or source at T_1 to the engine absorbing heat at T_1' , lower than T_1 . The availability of Q_1 as received by the engine at T_1' can be found by allowing the engine to operate reversibly in a cycle between T_1' and T_0 receiving Q_1 and rejecting Q_2' .

$$\text{Now, } Q_1 = T_1 \Delta s = T_1' \Delta s'$$

$$\text{— } T_1 > T_1'$$

$$\therefore \Delta s' > \Delta s$$

$$Q_2 = T_0 \Delta s$$

$$Q_2' = T_0 \Delta s'$$

$$\text{— } \Delta s' > \Delta s$$

$$\therefore Q_2' > Q_2$$

$$\therefore W' = Q_1 - Q_2' = T_1' \Delta s' - T_0 \Delta s' \text{ and } W = Q_1 - Q_2 = T_1 \Delta s - T_0 \Delta s$$

$$\therefore W' < W, \text{ because } Q_2' > Q_2$$

The loss of available energy due to irreversible heat transfer through finite temperature difference between the source and the working fluid during the heat addition process is given as :

$$W - W' = Q2' - Q2 = T0 (\Delta s' - \Delta s)$$

i.e., Decrease in available energy, A.E.

$$= T0 (\Delta s' - \Delta s)$$

Thus the decrease in A.E. is the product of the lowest feasible temperature of heat rejection and the additional entropy change in the system while receiving heat irreversibly, compared to the case of reversible heat transfer from the same source. The greater is the temperature difference ($T1 - T1'$), the greater is the heat rejection $Q2'$ and the greater will be the unavailable part of the energy supplied.

Energy is said to be degraded each time it flows through a finite temperature difference. That is, why the second law of thermodynamics is sometimes called the law of the degradation of energy, and energy is said to „run down hill“.

4.3 Availability in non-flow systems:

Let us consider a system consisting of a fluid in a cylinder behind a piston, the fluid expanding reversibly from initial condition of p_1 and T_1 to final atmospheric conditions of p_0 and T_0 . Imagine also that the system works in conjunction with a reversible heat engine which receives heat reversibly from the fluid in the cylinder such that the working substance of the heat engine follows the cycle O1LO as shown ,where $s_1 = s_1$ and $T_0 = T_L$ (the only possible way in which this could occur would be if an infinite number of reversible heat engines were arranged in parallel, each operating on a Carnot cycle, each one receiving heat at a different constant temperature and each one rejecting heat at T_0). The work done by the engine is given by :

$$W_{\text{engine}} = \text{Heat supplied} - \text{Heat rejected} = Q - T_0 (s_1 - s_0) \dots(i)$$

The heat supplied to the engine is equal to the heat rejected by the fluid in the cylinder. Therefore, for the fluid in the cylinder undergoing the process 1 to 0, we have

$$-Q = (u_0 - u_1) + W_{\text{fluid}}$$

$$\text{i.e., } W_{\text{fluid}} = (u_1 - u_0) - Q \dots(ii)$$

Adding eqns. (i) and (ii), we get

$$W_{\text{fluid}} + W_{\text{engine}} = [(u_1 - u_0) - Q] + [Q - T_0 (s_1 - s_0)]$$

$$= (u_1 - u_0) - T_0 (s_1 - s_0)$$

The work done by the fluid on the piston is less than the total work done by the fluid, since there is no work done on the atmosphere which is at constant pressure p_0

$$\text{i.e., Work done on atmosphere} = p_0 (v_0 - v_1)$$

Hence, maximum work available

$$= (u_1 - u_0) - T_0 (s_1 - s_0) - p_0 (v_0 - v_1)$$

Note. When a fluid undergoes a complete cycle then the net work done on the atmosphere is zero.

$$W_{\text{max}} = (u_1 + p_0 v_1 - T_0 s_1) - (u_0 + p_0 v_0 - T_0 s_0) \dots(6.3)$$

$$\therefore W_{\max} = a_1 - a_0$$

The property, $a = u + p_0 v - T_0 s$ (per unit mass) is called the non-flow availability function.

4.4 Helmholtz and gibbs functions:

The work done in a non-flow reversible system (per unit mass) is given by :

$$W = Q - (u_0 - u_1)$$

$$= T \cdot ds - (u_0 - u_1)$$

$$= T (s_0 - s_1) - (u_0 - u_1)$$

$$\text{i.e., } W = (u_1 - Ts_1) - (u_0 - Ts_0)$$

The term $(u - Ts)$ is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source. If work against atmosphere is equal to $p_0(v_0 - v_1)$, then the maximum work available,

$$W_{\max} = W - \text{work against atmosphere}$$

$$= W - p_0(v_0 - v_1)$$

$$= (u_1 - Ts_1) - (u_0 - Ts_0) - p_0(v_0 - v_1)$$

$$= (u_1 + p_0v_1 - Ts_1) - (u_0 + p_0v_0 - Ts_0)$$

$$= (h_1 - Ts_1) - (h_0 - Ts_0)$$

$$\text{i.e., } W_{\max} = g_1 - g_0$$

where $g = h - T \cdot s$ is known as Gibb's function or free energy function.

The maximum possible available work when system changes from 1 to 2 is given by

$$W_{\max} = (g_1 - g_0) - (g_2 - g_0) = g_1 - g_2$$

Similarly, for steady flow system the maximum work available is given by

$$W_{\max} = (g_1 - g_2) + (KE_1 - KE_2) + (PE_1 - PE_2)$$

where K.E. and P.E. represent the kinetic and potential energies.

It may be noted that Gibb's function $g = (h - Ts)$ is a property of the system where availability function $a = (u + p_0v - T_0s)$ is a composite property of the system and surroundings.

$$\text{Again, } a = u + p_0v - T_0s$$

$$b = u + pv - T_0s$$

$$g = u + pv - Ts$$

When state 1 proceeds to dead state (zero state)

$$a = b = g.$$

4.5. IRREVERSIBILITY:

The actual work which a system does is always less than the idealized reversible work, and the difference between the two is called the irreversibility of the process. Thus, Irreversibility, $I = W_{\max} - W \dots(6.8)$

This is also sometimes referred to as „degradation“ or „dissipation“.

For a non-flow process between the equilibrium states, when the system exchanges heat only with environment, irreversibility (per unit mass),

$$i = [(u_1 - u_2) - T_0(s_1 - s_2)] - [(u_1 - u_2) + Q]$$

$$= T_0 (s_2 - s_1) - Q$$

$$= T_0 (\Delta s)_{\text{system}} + T_0 (\Delta s)_{\text{surr.}}$$

$$\text{i.e., } i = T_0 [(\Delta s)_{\text{system}} + (\Delta s)_{\text{surr.}}] \dots(6.9)$$

$$\therefore i \geq 0$$

Similarly, for steady flow-process

$$i = W_{\text{max}} - W \text{ (per unit mass)}$$

$$= T_0 (s_2 - s_1) - Q$$

$$= T_0 (\Delta s)_{\text{system}} + T_0 (\Delta s)_{\text{surr.}}$$

$$\text{i.e., } i = T_0 (\Delta s_{\text{system}} + \Delta s_{\text{surr.}})$$

The same expression for irreversibility applies to both flow and non-flow processes.

The quantity $T_0 (\Delta s_{\text{system}} + \Delta s_{\text{surr.}})$ represents (per unit mass) an increase in unavailable energy (or energy).

MODULE IV

THE PURE SUBSTANCE

OBJECTIVE: Introduce the concept of a pure substance and Illustrate the P-v , T-v and P-T property diagrams and P-v-T surfaces of pure substances. Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.

STRUCTURE:

4. Introduction

4.1 Application of 1st law of thermodynamics for a closed system

4. Introduction: 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.

“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.”

Pure Substances

Define Pure Substance:

A substance that has a fixed chemical composition throughout is called a pure substance such as water, air, and nitrogen.

A pure substance does not have to be of a single element or compound. A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.

Phases of a Pure Substance

A pure substance may exist in different phases. There are three principal phases solid, liquid, and gas.

A phase: is defined as having a distinct molecular arrangement that is homogenous throughout and separated from others (if any) by easily identifiable boundary surfaces.

A substance may have several phases within a principal phase, each with a different molecular structure. For example, carbon may exist as graphite or diamond in the solid phase, and ice may exist in seven different phases at high pressure.

Molecular bonds are the strongest in solids and the weakest in gases.

Solid: the molecules are arranged in a three-dimensional pattern (lattice) throughout the solid. The molecules cannot move relative to each other; however, they continually oscillate about their equilibrium position.

Liquid: the molecular spacing in liquid phase is not much different from that of the solid phase (generally slightly higher), except the molecules are no longer at fixed positions relative to each other.

Gas: the molecules are far apart from each other, and a molecular order does not exist. Gas molecules move randomly, and continually collide with each other and the walls of the container they are in.

Molecules in the gas phase are at a considerably higher energy level than they are in liquids or solid phases

Phase-Change Processes of Pure Substances:

Consider a process where a pure substance starts as a solid and is heated up at constant pressure until it all becomes gas. Depending on the prevailing pressure, the matter will pass through various phase transformations. At P_0 :

1. Solid
2. Mixed phase of liquid and solid
3. Sub-cooled or compressed liquid (means it is not about to vaporize)
4. Wet vapor or saturated liquid- vapor mixture, the temperature will stop rising until the liquid is completely vaporized.
5. Superheated vapor

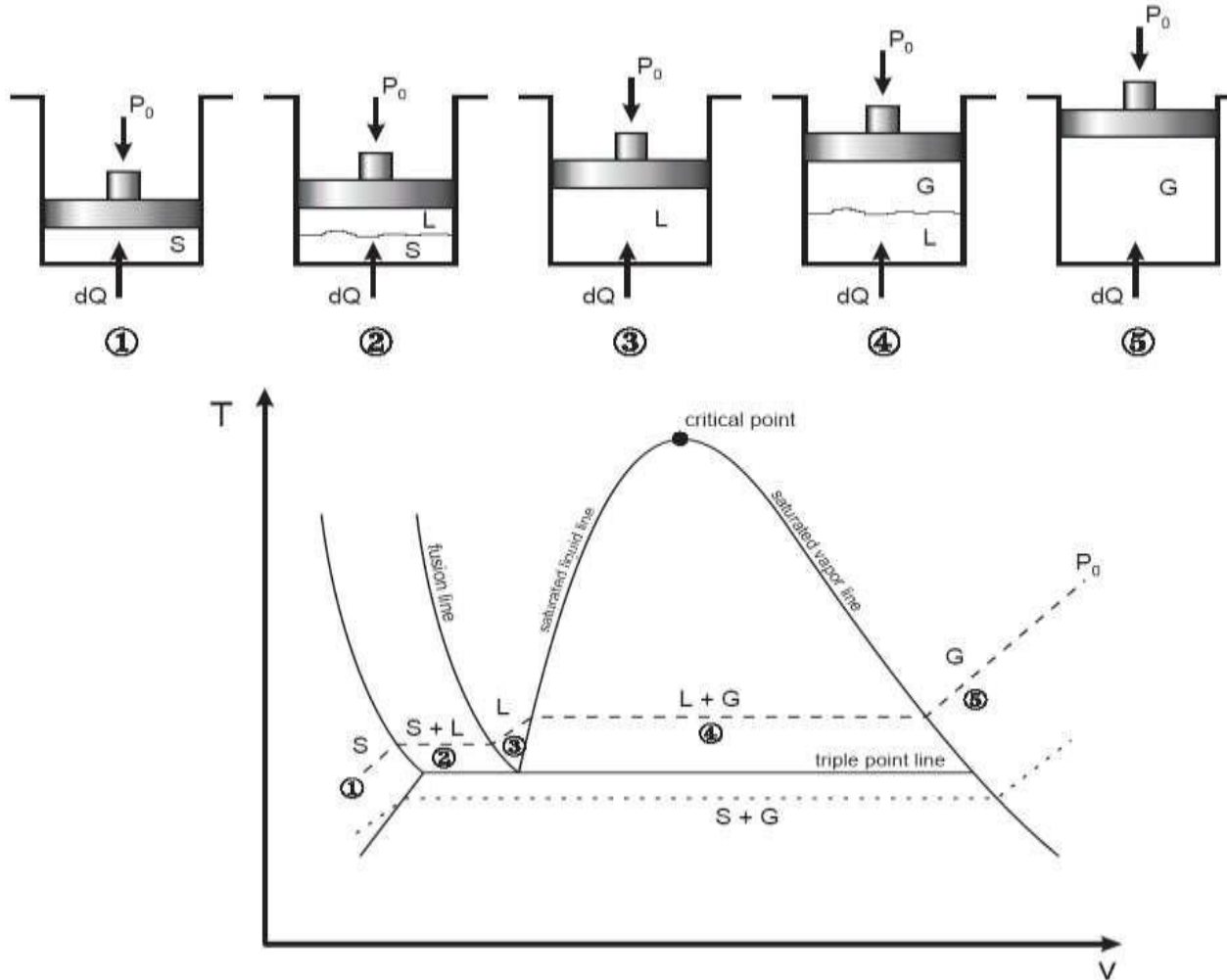


Fig. 1: T-v diagram for the heating process of a pure substance.

- ◆ At a given pressure, the temperature at which a pure substance starts boiling is called the saturation temperature, T_{sat} .
- ◆ Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the saturation pressure, P_{sat} .
- ◆ During a phase-change process, pressure and temperature are dependent properties, $T_{\text{sat}} = f(P_{\text{sat}})$.

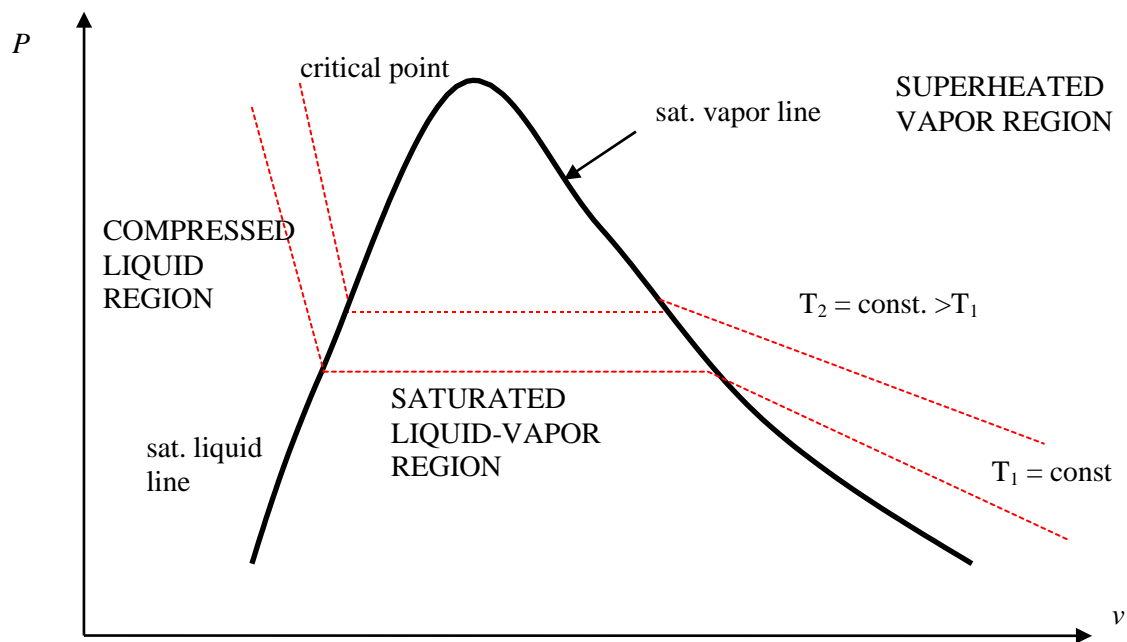
- ◆ The critical point is the point at which the liquid and vapor phases are not distinguishable
- ◆ The “triple point” is the point at which the liquid, solid, and vapor phases can exist together. On P-v or T-v diagrams, these triple-phase states form a line called the triple line.

Table 1: Critical and triple point for water and oxygen.

	Critical Point		Triple Point	
	P (atm)	T (K /°C)	P (atm)	T (K /°C)
H ₂ O	218	647.30/(374.14)	0.006	273.17 (0.01)
O ₂	50.136	154.80/(-118.36)	0.0015	54.16/(-219)

Vapor Dome

The general shape of a P-v diagram for a pure substance is very similar to that of a T-v diagram.

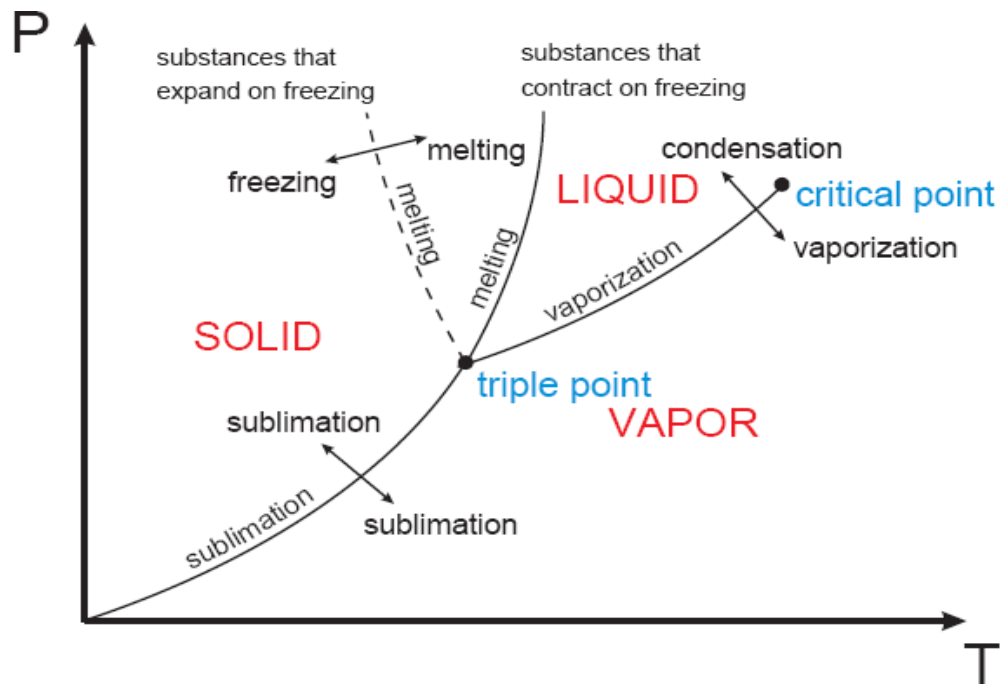


P-v diagram of a pure substance.

The P-T or Phase Change Diagram

This is called phase diagram since all three phases are separated from each other by three lines. Most pure substances exhibit the same behavior.

- ◆ One exception is water. Water expands upon freezing.



Phase diagram of pure substances.

There are two ways that a substance can pass from solid phase to vapor phase i) it melts first into a liquid and subsequently evaporates, ii) it evaporates directly without melting (sublimation).

- ◆ the sublimation line separates the solid and the vapor.
- ◆ the vaporization line separates the liquid and vapor regions
- ◆ the melting or fusion line separates the solid and liquid.
- ◆ these three lines meet at the triple point.
 - if $P < P_{TP}$, the solid phase can change directly to a vapor phase
 - at $P < P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P > P_{TP}$) the substance melts into a liquid and then evaporates.
 - matter (like CO_2) which has a triple point above 1 atm sublimate under atmospheric conditions (dry ice)
 - for water (as the most common working fluid) we are mainly interested in the liquid and vapor regions. Hence, we are mostly interested in boiling and condensation.

Property Tables

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Thus, properties are frequently presented in the form of tables, see Table A-4.

The subscript “f” is used to denote properties of a saturated liquid and “g” for saturated vapor. Another subscript, “fg”, denotes the difference between the saturated vapor and saturated liquid values of the same property.

For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f ($v_{fg} = v_g - v_f$)

Enthalpy: is a property defined as $H = U + PV$ (kJ) or $h = u + Pv$ (kJ/kg) (per mass unit).

Enthalpy of vaporization (or latent heat): represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increase, and becomes zero at the critical point.

1- Saturated Liquid-Vapor Mixture

During vaporization, a mixture of part liquid part vapor exists. To analyze this mixture, we need to know the proportions of the liquid and vapor in the mixture. The ratio of the mass of vapor to the mass of the total mixture is called quality, x :

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \quad m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Saturated liquid-vapor mixture is treated as a combination of two sub-systems (two phases). The properties of the “mixture” are the average properties of the saturated liquid-vapor mixture.

$$V = V_f + V_g$$

$$m_t v_{ave} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \rightarrow m_t v_{ave} = (m_t - m_g) v_f + m_g v_g$$

dividing by m_t

$$v_{ave} = (1 - x) v_f + x v_g \quad \text{and} \quad x = m_g / m_t$$

$$v_{ave} = v_f + x v_{fg} \quad (m^3 / kg)$$

or,

$$x = \frac{v_{ave} - v_f}{v_{fg}}$$

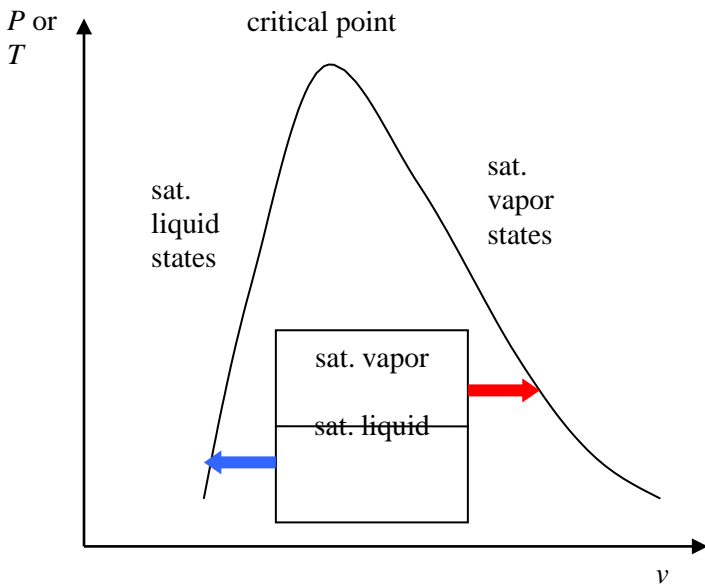


Fig. 4: The relative amounts of liquid and vapor phases (quality x) are used to calculate the mixture properties.

Similarly,

$$u_{ave} = u_f + xu_{fg}$$

$$h_{ave} = h_f + xh_{fg}$$

Or in general, it can be summarized as $y_{ave} = y_f + x \cdot y_{fg}$. Note that:

$$0 \leq x \leq 1$$

$$y_f \leq y_{ave} \leq y_g$$

Note: pressure and temperature are dependent in the saturated mixture region.

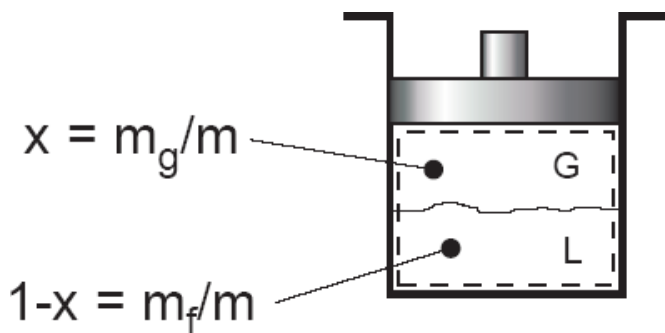


Fig. 5: Quality defined only for saturated liquid-vapor mixture.

Example 1: Saturated liquid-vapor mixture

A closed, rigid container of volume 0.5 m^3 is placed on a hot plate. Initially the container holds a two-phase mixture of saturated liquid water and saturated water vapor at $P_1 = 1 \text{ bar}$ with a quality of 0.5. After heating, the pressure in the container is $P_2 = 1.5 \text{ bar}$. Indicate the initial and final states on a T-v diagram, and determine:

- the temperature, in $^\circ\text{C}$, at each state.
- the mass of vapor present at each state, in kg.
- if heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

Solution:

Assumptions:

- Water in the container is a closed system.
- States 1, 2, and 3 are equilibrium states.
- The volume of container remains constant.

Two independent properties are required to fix state 1 and 2. At the initial state, the pressure and quality are known. Thus state 1 is known, as mentioned in the problem. The specific volume at state 1 is found using the given quality:

$$v_1 = v_{f1} + x_1(v_{g1} - v_{f1})$$

From Table A - 5 at $P = 1 \text{ bar} = 100 \text{ kPa}$

$$v_1 = 0.001043 + 0.5(1.694 - 0.001043) = 0.8475 \text{ m}^3 / \text{kg}$$

At state 2, the pressure is known. Volume and mass remain constant during the heating process within the container, so $v_2 = v_1$. For $P_2 = 0.15 \text{ MPa}$, Table A-5 gives $v_{f2} = 0.001053$ and $v_{g2} = 1.1593 \text{ m}^3/\text{kg}$. Since

$$v_{f2} < v_2 < v_{g2}$$

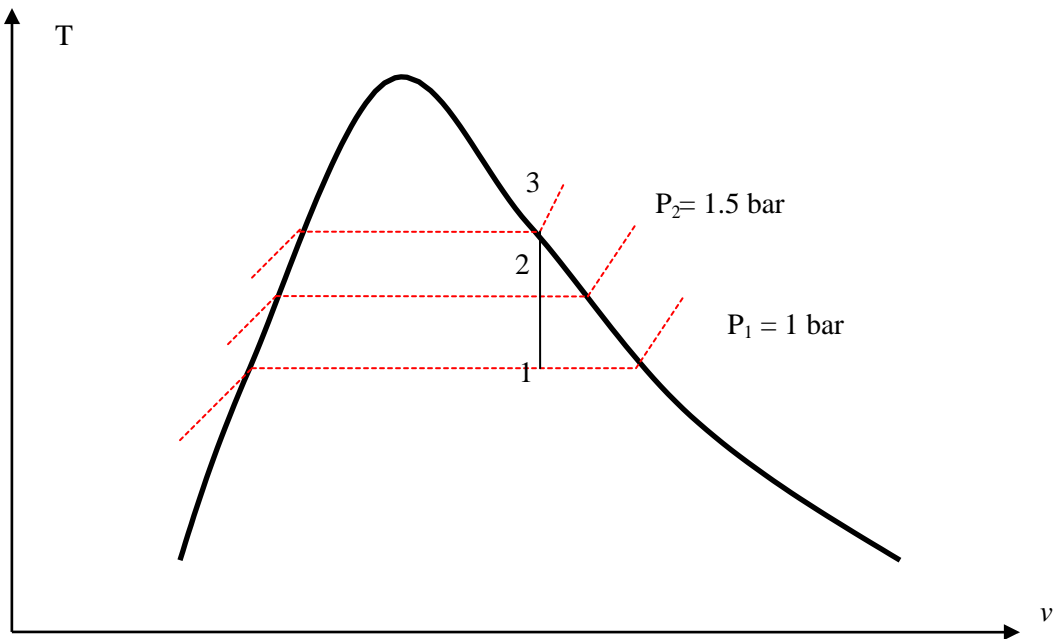
State 2 must be in the two-phase region as well. Since state 1 and 2 are in the two-phase liquid-vapor region, the temperatures correspond to the saturation temperatures for the given. Table A-5:

$$T_1 = 99.63 \text{ }^\circ\text{C} \text{ and } T_2 = 111.4 \text{ }^\circ\text{C}$$

To find the mass of water vapor present, we first find the total mass, m .

$$m = \frac{V}{v} = \frac{0.5 \text{ m}^3}{0.8475 \text{ m}^3 / \text{kg}} = 0.59 \text{ kg}$$

$$m_{g1} = x_1 m = 0.5(0.59 \text{ kg}) = 0.295 \text{ kg}$$



The mass of vapor at state 2 is found similarly using quality x_2 . From Table A-5, for $P_2 = 1.5$ bar, we have:

$$x_2 = \frac{v - v_{f2}}{v_{g2} - v_{f2}}$$

$$x_2 = \frac{0.8475 - 0.001053}{1.159 - 0.001053} = 0.731$$

$$m_{g2} = 0.731 (0.59 \text{ kg}) = 0.431 \text{ kg}$$

If heating continued, state 3 would be on the saturated vapor line, as shown in on the T-v diagram above. Thus, the pressure would be the corresponding saturation pressure. Interpolating in Table A-5 at $v_g = 0.8475 \text{ m}^3/\text{kg}$, we get $P_3 = 2.11$ bar.

2- Superheated Vapor

Superheated region is a single phase region (vapor only), temperature and pressure are no longer dependent. See Table A-6 for superheated vapor properties.

If $T \gg T_{\text{critical}}$ or $P \ll P_{\text{critical}}$, then the vapor can be approximated as an “ideal gas”.

3- Compressed (or Sub-cooled) Liquid

The properties of a liquid are relatively independent of pressure (incompressible).

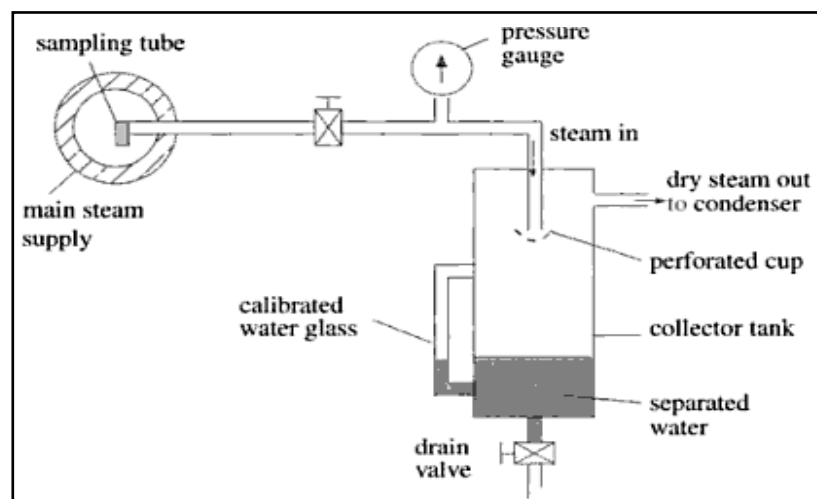
A general approximation is to treat compressed liquid as saturated liquid at the given saturation temperature.

Determination the dryness fraction:

- **Separating calorimeter:**

The quality of wet steam is usually defined by its dryness fraction. When the dryness fraction, pressure and temperature of the steam are known, then the state of wet steam is fully defined. In a steam plant it is at times necessary to know the state of the steam. For wet steam, this entails finding the dryness fraction. When the steam is very wet, we make use of a separating calorimeter.

Construction of separating calorimeter is as shown in figure:



The steam is collected out of the main steam supply and enters the separator from the top. The steam is forced to make a sharp turn when it hits the perforated cup (or any other mechanism that produces the same effect). This results in a vortex motion in the steam, and water separates out by the centrifugal action. The droplets then remain inside the separator and are collected at the bottom, where the level can be recorded from the water glass. The dry steam will pass out of the calorimeter into a small condenser for the collection of the condensate. However, not all the water droplets remain in the collector tank. Some water droplets pass through to the condenser, and hence this calorimeter only gives a close approximation of the dryness fraction of the steam.

- **Throttling calorimeter:**

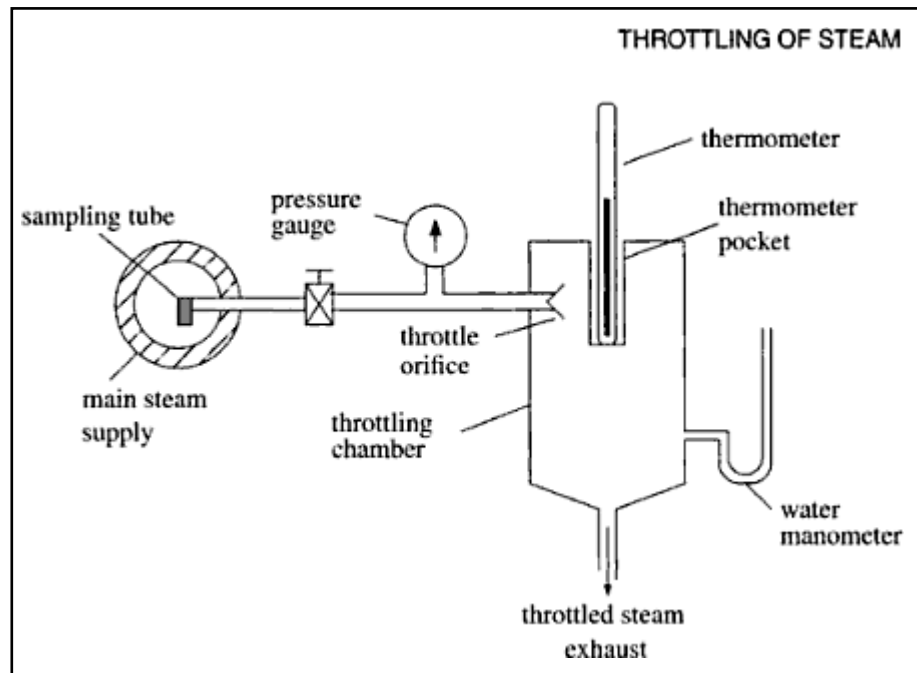
If we have steam that is nearly dry, we make use of a throttling calorimeter as shown in figure. This calorimeter is operated by first opening the stop valve fully so that the steam is not partially throttled as it passes through the apparatus for a while to allow the pressure and temperature to stabilize. If the pressure is very close to atmospheric pressure, the saturation should be around 100°C , it may be assumed that the steam is superheated.

When the conditions have become steady, the gauge pressure before throttling is read from the pressure gauge. After throttling, the temperature and gauge pressure are read from the thermometer and manometer respectively. The barometric pressure is also recorded.

From equation $h_1 = h_2$,

We have h_w at $p_1 = h_{sup}$ at p_2

And thus $x = \frac{h_{g2} + Cp (T_{sup} - T_{sat}) - h_{f1}}{h_{fg1}}$



List of Formulas:

1. Dryness fraction of steam sample entering Separating Calorimeter = $x = \frac{M}{M+m}$ ———

Where, M is the mass of dry steam and

m is the mass of suspended water separated in the calorimeter in the same time.

2. Dryness fraction of steam sample entering Throttling calorimeter

We have h_w at $p_1 = h_{sup}$ at p_2

$$\text{And thus } x = \frac{h_{g2} + C_p (T_{sup} - T_{sat}) - h_{f1}}{h_{fg1}}$$

3. Dryness Fraction = $x = \frac{\text{Mass of dry steam}}{\text{Mass of wet steam}}$

4. Specific Enthalpy of wet steam at Pressure $P = h = h_f + x h_{fg}$ KJ/Kg (Similarly specific entropy, specific volume can be calculated)

5. Enthalpy(h) = Internal energy(u) + ($P.v$)

6. Specific heat at constant volume = $C_v = du/dt$

7. Specific heat at constant pressure = $C_p = dh/dt$

8. Specific heat at constant pressure for dry steam = $C_{ps} = 2.1 \text{ KJ/Kg.K}$

OUTCOME: Demonstrate understanding of key concepts including phase and pure substance, state principle for simple compressible systems, p-v-T surface, saturation temperature and saturation pressure, two-phase liquid-vapor mixture, quality, enthalpy, and specific heats. Apply the closed system energy balance with property data.

IMPORTANT QUESTIONS:

1. With a neat sketch explain how Combined separating and throttling calorimeter can be used to measure the dryness fraction of wet vapour
2. With a neat sketch explain throttling calorimeter can be used to measure the dryness fraction of wet vapour
3. Draw phase equilibrium diagram of water on P-T Coordinates indicating triple and critical point
4. Steam initially at 1.5 MPa 300°C expands reversibly and adiabatically in a steam turbine to 40°C . Determine the ideal work output of the turbine per kg of steam

FURTHER READING:

1. Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
2. Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
3. <http://www.nptel.ac.in/courses/112104113/4#>

Problems

Question paper problems

Steam initially at 1.5 Mpa, 300°C expands reversibly & adiabatically in a steam turbine to 40°C. Determine the ideal work output of the turbine per kg of steam.

→ SFEE for the control volume

$$\begin{aligned} \text{for Turbine } d(K.E) &= 0 \\ d(P.E) &= 0 \\ W &\text{ is +ve} \\ Q &= 0 \text{ (adiabatic)} \end{aligned}$$

$$\therefore W = (h_1 - h_2)$$

The process is reversible & adiabatic, so it is isentropic hence the line 1-2 will be vertical in T-s & h-s diagram.

From steam table (15 bar)

since at $P_1 = 1.5 \text{ Mpa}$, $T_1 = 300^\circ\text{C}$

$T_1 > T_s$ (saturation temperature) hence

we have to check $P_2 = 15 \text{ bar}$, $T = 300^\circ\text{C}$ in superheated steam table for properties at state 1 (superheated condition)

$$h_1 = 3038.9 \text{ kJ/kg} = h_{\text{sup}}$$

$$s_1 = 6.9207 \text{ kJ/kg}\cdot\text{K} = s_{\text{sup}}$$

for state 2 :- (Liquid vapour mixture region)

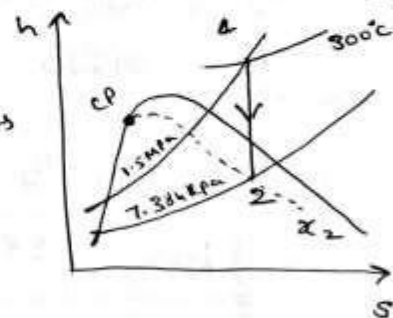
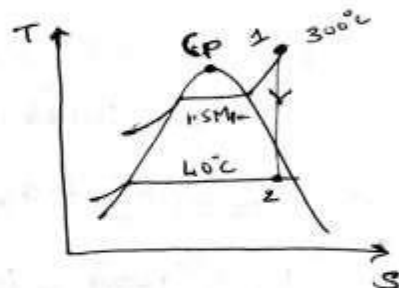
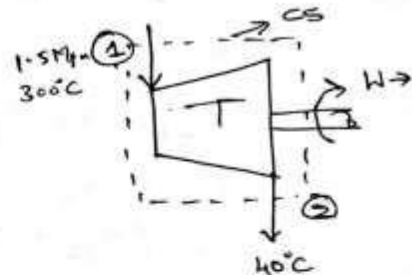
$$P_2 = P_{\text{saturation}} = 0.073750 \text{ bar} = 7.375 \text{ kPa}$$

$$s_f = 0.5721 \text{ kJ/kg}\cdot\text{K}$$

$$h_f = 167.5 \text{ kJ/kg}$$

$$s_{fg} = 7.6845 \text{ kJ/kg}\cdot\text{K}$$

$$h_{fg} = 2406.9 \text{ kJ/kg}$$



To find h_2

$$h_2 = h_{g2} + x_2 h_{fg2}$$

To find x_2 which is unknown
we have $S_1 = S_2$ (adiabatic expansion)

$$S_1 = 6.9207 \text{ kJ/kg K}$$

$$S_2 = S_{g2} + x_2 S_{fg2}$$

$$S_1 = S_2$$

$$6.9207 = (S_{g2} + x_2 S_{fg2})_{40^\circ\text{C}}$$

$$6.9207 = 0.5721 + x_2 \times 7.6845$$

$$x_2 = 0.826 \text{ or } 82.6\%$$

$$\therefore h_2 = (h_{g2} + x_2 h_{fg2})_{40^\circ\text{C}}$$

$$h_2 = (167.5 + (0.826 \times 2406.9))$$

$$h_2 = 2152.57 \text{ kJ/kg}$$

$$\therefore W = h_1 - h_2 = (3038.9 - 2152.57) = 885.03 \text{ kJ/kg} //$$

$$\boxed{W = +885.03 \text{ kJ/kg}}$$

2) A rigid vessel of 2 m^3 volume is filled with super heated steam at 20 bar & 300°C . The vessel is cooled until the steam is just dry saturated. Calculate the mass of steam in the vessel, the final pressure of steam & the amount of energy transferred as heat to the surroundings. Represent the process on T-s diagram

Solution:-

At state point 1,

$$P_1 = 20 \text{ bar}, T_1 = 300^\circ\text{C}, V_1 = 2 \text{ m}^3$$

From steam table

superheated steam table

$$P_1 = 20 \text{ bar}, T_1 = 300^\circ\text{C}$$

$$\text{Specific volume: } v_{\text{sup}} = v_1 = 0.12550 \text{ m}^3/\text{kg}$$

Mass of steam in vessel

$$m = \frac{V_1}{v_1} = \frac{2}{0.12550} = 16 \text{ kg}$$

Since the tank is rigid the volume remains constant

$$\therefore v_2 = v_1 = 0.12550 \text{ m}^3/\text{kg}$$

The steam is just dry & saturated at point 2 & so

$$v_{g2} = v_2 = 0.12550 \text{ m}^3/\text{kg}$$

From steam tables, the pressure of dry saturated steam corresponding to specific volume $0.125 \text{ m}^3/\text{kg}$ is 16 bar

For constant volume process, workdone is zero & therefore from the principle of energy conservation

$$\text{heat transferred} = q_2 = du = u_2 - u_1$$

$$q_2 = (h_2 - P_2 v_2) - (h_1 - P_1 v_1)$$

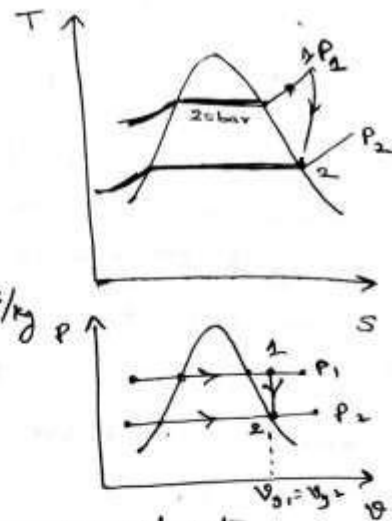
$$= (h_2 - h_1) - v_1 (P_2 - P_1) \quad \{ \because v_2 = v_1 \}$$

$$\text{At } 20 \text{ bar \& } 300^\circ\text{C} \quad h_1 = 3023.9 \text{ kJ/kg}$$

$$\text{At } 16 \text{ bar \& } x=1 \quad h_2 = h_g = 2791.7 \text{ kJ/kg (dry saturated)}$$

$$\therefore q_2 = (2791.7 - 3023.9) - [0.12550 (16 - 20) \times 10^5]$$

$$q_2 = -182.4 \text{ kJ/kg}$$



∴ Total energy transferred as heat to Surroundings

$$Q_2 = m \cdot q_{12} = 16 (-82.4) = \underline{\underline{-1318.4 \text{ kJ}}}$$

⇒ calculate the internal energy per kg of superheated steam at pressure of 10 bar & a temperature of 300°C. Also find the change in internal energy if this steam is expanded to 1.4 bar & dryness fraction 0.8

→ state 1 :- $P_1 = 10 \text{ bar}$, $T_1 = T_{\text{sup}} = 300^\circ\text{C}$

state 2 :- $P_2 = 1.4 \text{ bar}$, $x_2 = 0.8$

To find u_1

$u_1 = h_1 - P_1 v_{g1}$ {superheated steam}
from superheated steam table

$$h_1 = 3052.1 \text{ kJ/kg}, v_{g1}$$

v_{g1} at $P_1 = 10 \text{ bar}$ from ~~superheated~~ ^{superheated} steam table

$$v_{g1} = v_{g \text{ sup}} = 0.25798 \text{ m}^3/\text{kg}$$

$$\therefore u_1 = 3052.1 - (10 \times 10^2 \times 0.25798)$$

$$u_1 = 2794.12 \text{ kJ/kg}$$

To find u_2

$$u_2 = h_2 - x_2 P_2 v_{g2}$$

$$u_2 = (h_{f2} + x_2 h_{fg2}) - x_2 P_2 v_{g2}$$

• at $P_2 = 1.4 \text{ bar}$ from Saturated steam table

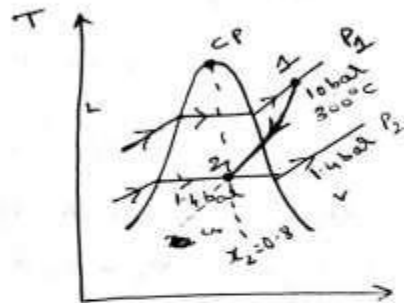
$$h_{f2} = 458.4 \text{ kJ/kg}, x_2 = 0.8 \text{ (Given)}$$

$$h_{fg2} = 2231.9 \text{ kJ/kg}, P_2 = 1.4 \times 10^2 \text{ kPa}$$

$$v_{g2} = 1.2363$$

$$\therefore u_2 = 2105.4544 \text{ kJ/kg}$$

$$\text{Change in internal energy} = u_2 - u_1 = 688.66 \text{ kJ/kg}$$



Process 1-2 represents
the expansion process

4) The following data were obtained with a separating & throttling calorimeter
 pressure in pipeline = 1.5 MPa

Condition after throttling = 0.1 MPa, 110°C

During 5 min, moisture collected in the separator = 0.15 kg at 70°C

steam condensed after throttling during 5 min = 3.24 kg

Find the quality of steam in the pipe line

→ Let m_1 = mass of moisture collected in a separator in 5 min
 & m_2 = mass of steam condensed after throttling in 5 min

$$\text{then } x_1 = \frac{x_2 m_2}{m_1 + m_2}$$

from h-s diagram & steam table

To find x_2 :-

at state 3, at 0.1 MPa & 110°C

$$h_3 = 2696.2 \text{ kJ/kg}$$

we know that for a throttling process
 enthalpy at inlet = enthalpy at outlet

$$h_2 = h_3 =$$

$$(h_f + x_2 h_{fg})_{1.5 \text{ MPa}} = h_3 = 2696.2$$

$$844.87 + x_2 \times 1947.3 = 2696.2$$

$$\boxed{x_2 = 0.955}$$

To find m_1 :-

at 70°C moisture collected in the

$$\text{separator} = V_1 = 0.150 \text{ kg} = 0.150 \times 10^{-3} \text{ m}^3$$

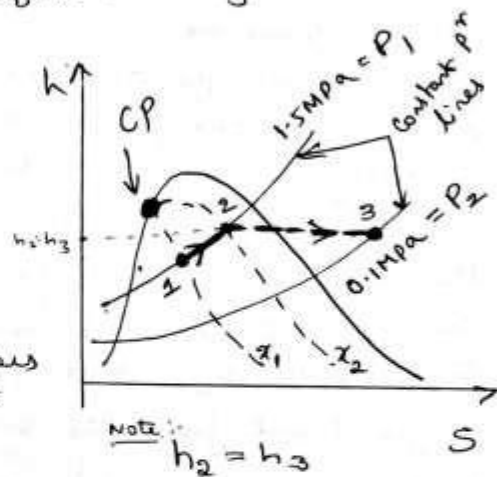
To convert m^3 to kg

$$\text{at } 70^\circ\text{C}, v_f = 0.001023 \text{ m}^3/\text{kg}$$

$$\therefore m_1 = \frac{0.150 \times 10^{-3} \text{ m}^3}{0.001023 \text{ m}^3/\text{kg}} = 0.1462 \text{ kg}$$

$$m_2 = 3.24 \text{ kg (Given)}$$

$$\therefore \boxed{x_1 = 0.915}$$



\Rightarrow Steam flows in a pipeline at 1.5 MPa. After expanding to 0.1 MPa in a throttling calorimeter, the temperature is found to be 120°C. Find the quality of steam in the pipeline. What is the maximum moisture at 1.5 MPa that can be determined with this setup if at least 5% of superheat is required after throttling for accurate readings?

\rightarrow At state 2, when $P = 0.1 \text{ MPa}$, $t = 120^\circ\text{C}$ by interpolation

superheated table by interpolation we get

$$h_2 = 2716.2 \text{ kJ/kg}$$

At pressure 1.5 MPa = 15 bar from saturated steam table

$$h_f = 844.89 \text{ kJ/kg} \quad h_{fg} = 1947.3 \text{ kJ/kg}$$

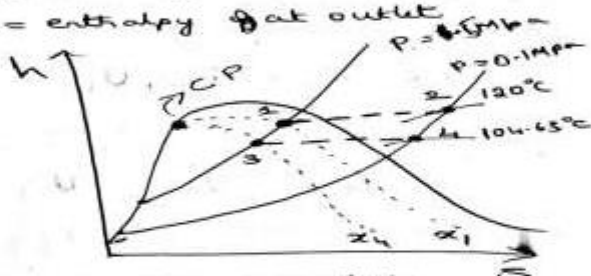
To find x_1 , we know that across throttling valve during throttling process enthalpy at inlet = enthalpy at outlet

$$\therefore h_1 = h_2$$

$$[h_f + x_1 h_{fg}]_{P=15 \text{ bar}} = 2716.2$$

$$844.89 + x_1 \times 1947.3 = 2716.2$$

$$\boxed{x_1 = 0.963}$$



To find x_2 :-

It is given that the exit temperature is 5°C more than the saturation temperature at pressure $P_2 = 0.1 \text{ MPa} = 1 \text{ bar}$

Temperature at exit of the valve for condition 2 is

at $P = 1 \text{ bar}$ from saturated steam table $T_s = 99.63$

\therefore Exit temperature = superheated temperature = $99.63 + 5$ at exit

$$T_{\text{sup}} \text{ for condition 2} = 104.63^\circ\text{C}$$

\therefore from superheated steam table at 1 bar & 104.63°C

$$h_{\text{sup}} = h_2 = 2685.5 \text{ kJ/kg}$$

Since $h_1 = h_2$

$$2685.5 = [h_f + x_2 h_{fg}]_{P=1 \text{ bar}}$$

from saturated steam table

$$2685.5 = 844.89 + x_2 \times 1947.3$$

$$x_2 = 0.9218$$

$$\left. \begin{aligned} \text{dryness fraction} &= 0.948 \\ &= 94.8\% \end{aligned} \right\}$$

$$\left. \begin{aligned} \text{moisture fraction} &= 1 - 0.948 \\ &= 0.052 \\ &= 5.2\% \end{aligned} \right\}$$

The maximum moisture that can be determined with the setup = 5.2%

6) A steam boiler initially contains 5 m^3 of steam & 5 m^3 of water at 1 Mpa . Steam is taken out at constant pressure until 4 m^3 of water is left. What is the heat transferred during the process

$$\rightarrow \left\{ \begin{array}{l} \text{heat transferred} \\ \text{during the process} \end{array} \right\} = \left\{ \begin{array}{l} \text{Final energy} \\ \text{stored in saturated} \\ \text{water \& steam} \end{array} \right\} - \left\{ \begin{array}{l} \text{Initial} \\ \text{energy} \\ \text{stored} \end{array} \right\} + \left\{ \begin{array}{l} \text{Energy going} \\ \text{out with} \\ \text{steam removed} \\ \text{of } (m_s) \text{ mass} \end{array} \right\}$$

$$Q = (m_2 U_2 - m_1 U_1) + m_s h_g$$

Assuming that steam taken out is dry ($x=1$) $\therefore Q_s = m_s h_g$
or we can write:-

$$Q (m_2 U_2 - m_1 U_1) = Q_s - m_s h_g \rightarrow \textcircled{1}$$

$$\left\{ \begin{array}{l} \text{change in internal energy} \end{array} \right\} = \left\{ \begin{array}{l} \text{heat input} \\ \text{to the system} \\ \text{from external} \\ \text{source} \end{array} \right\} - \left\{ \begin{array}{l} \text{heat or energy leaving} \\ \text{with dry steam} \end{array} \right\}$$

At $1 \text{ Mpa} = 10 \text{ bar}$ from saturated steam table

$$v_f = 0.001127, \quad v_g = 0.1944 \text{ m}^3/\text{kg}, \quad h_g = 2778.1 \text{ kJ/kg}$$

To find m_s :-

~~To find m_s~~ , The initial mass of saturated water & steam in the boiler is given by, at 10 bar $v_{f1} = 0.001127 \text{ m}^3/\text{kg}$
 $v_{g1} = 0.1944 \text{ m}^3/\text{kg}$

$$m_{f1} = \frac{V_{f1}}{v_{f1}} = \frac{5}{0.001127} = 4436.5 \text{ kg}$$

$$m_{g1} = \frac{V_{g1}}{v_{g1}} = \frac{5}{0.1944} = 25.72 \text{ kg}$$

\therefore The final mass of saturated water & steam in the boiler is given by

$$m_{f2} = \frac{V_{f2}}{v_{f2}} = \frac{4}{0.001127} = 3549.2 \text{ kg}$$

$$m_{g2} = \frac{V_{g2}}{v_{g2}} = \frac{6}{0.1944} = 30.86 \text{ kg}$$

\therefore pressure is constant

\therefore at $P = 10 \text{ bar}$

$$v_{f2} = v_{f1}$$

$$v_{g2} = v_{g1}$$

Mass of steam taken out of the boiler (m_s)
 = Total mass of mixture at state 1 - Total mass of mixture at state 2

$$= (m_{g1} + m_{g1}) - (m_{g2} + m_{g2})$$

$$m_s = \cancel{894.9 \text{ kg}} \quad 882.16 \text{ kg}$$

Equation (1) can be written as

$$U_2 - U_1 = Q - m_s h_g$$

$$[U_{f2} + U_{g2}] - [U_{f1} + U_{g1}] = Q - m_s h_g$$

$$(m_{f2} u_{f2} + m_{g2} u_{g2}) - (m_{f1} u_{f1} + m_{g1} u_{g1}) = Q - m_s h_g \rightarrow (3)$$

to find $u_{f2} = h_{f2} - P v_{f2} = 762.6 - 1.127 = 761.473 \text{ kJ/kg}$

$$u_{f1} = h_{f1} - P v_{f1} = 761.473 \text{ kJ/kg}$$

$$u_{g2} = h_{g2} - P v_{g2} = 2776.2 - 0.1944 = 2581.8 \text{ kJ/kg}$$

$$u_{g1} = h_{g1} - P v_{g1} = 2581.8 \text{ kJ/kg}$$

Substituting in (3) we get

$$(3549.2 \times 761.473 + 30.86 \times 2581.8) - (4436.5 \times 761.473 + 25.72 \times 2581.8) = Q - 882.16 \times 2778.1$$

$$\boxed{Q = 1752.676 \text{ MJ}} = 1.805 \text{ KJ} //$$

Avogadro's Law

“The volume of 1-gram mol of all gases at the pressure of 760 mm of Hg and temperature 0°C is the same and is equal to 22.4 liters.”

Ideal Gas

A gas which obeys the law $p\bar{v} = \bar{R}T$ at all pressures and temperatures is called an ideal gas.

$$\bar{v} = \frac{V}{n}$$
$$n = \frac{m}{\mu}$$

p = Pressure = 760 mm of Hg = 1.013×10^5 Pa

\bar{v} = Molar Volume = 22.4 litres

V = Total Volume (m^3)

T = Temperature = 0°C = 273.15K

n = No. of Moles

m = Total Mass (kg)

μ = Molecular Weight

Universal Gas Constant

$$\bar{R} = \frac{p\bar{v}}{T} = \frac{1.013 \times 10^5 \times 22.4}{273.15} = 8.314 \frac{\text{kJ}}{\text{kg mol K}}$$

\bar{R} = Universal Gas Constant

Characteristic Gas Constant

Now,

$$pV = nRT = \frac{m}{\mu}RT = m \frac{\bar{R}}{\mu} T = mRT$$

R = Characteristic Gas Constant

$$R_{O_2} = \frac{8.314}{32} = 0.262 \left(\frac{\text{kJ}}{\text{kgK}} \right)$$

$$R_{air} = \frac{8.314}{28.96} = 0.287 \left(\frac{\text{kJ}}{\text{kgK}} \right)$$

There are 6.023×10^{23} molecules in a gram mole of a substance.

Assumptions for an ideal gas

- There is little or no attraction between the molecules of the gas.
- The volume occupied by the molecules themselves is negligibly small compared to the volume of the gas.

When $p \rightarrow 0$ or $T \rightarrow \infty$, the intermolecular attraction and volume of the molecules are insignificant and real gas obeys the ideal gas equation

Specific Heats, Internal Energy and Enthalpy of an Ideal Gas

$$Tds = du + pdv$$

$$ds = \frac{1}{T} du + \frac{1}{T} pdv$$

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

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

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

$$= \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T} \left(\frac{\partial u}{\partial v}\right)_T dv + \frac{p}{T} dv$$

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

If, $s = (T, v)$,

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

Equating the coefficients of the terms in the equation for ds ,

Equating the coefficient of the term for dT gives,

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v \quad (1)$$

Equating the coefficient of the term for dv gives,

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T} \left[\left(\frac{\partial u}{\partial v}\right)_T + p \right] \quad (2)$$

Differentiating (1) wrt v when T is a constant,

$$\frac{\partial^2 s}{\partial T \partial v} = \frac{1}{T} \frac{\partial^2 u}{\partial T \partial v} \quad (3)$$

Differentiating (2) wrt T when v is a constant,

$$\begin{aligned} \frac{\partial^2 s}{\partial T \partial v} &= \frac{1}{T} \cdot \frac{\partial}{\partial T} \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] + \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] \cdot \frac{\partial}{\partial T} \left(\frac{1}{T} \right) \\ &= \frac{1}{T} \frac{\partial^2 u}{\partial T \partial v} + \frac{1}{T} \left(\frac{\partial p}{\partial T} \right)_v - \frac{1}{T^2} \left(\frac{\partial u}{\partial v} \right)_T - \frac{p}{T^2} \end{aligned} \quad (4)$$

(3) = (4),

$$\begin{aligned} \frac{1}{T} \frac{\partial^2 u}{\partial T \partial v} &= \frac{1}{T} \frac{\partial^2 u}{\partial T \partial v} + \frac{1}{T} \left(\frac{\partial p}{\partial T} \right)_v - \frac{1}{T^2} \left(\frac{\partial u}{\partial v} \right)_T - \frac{p}{T^2} \\ \left(\frac{\partial u}{\partial v} \right)_T + p &= T \left(\frac{\partial p}{\partial T} \right)_v \end{aligned}$$

For an ideal gas, $pv = RT$

Differentiating the ideal gas equation wrt T when v is constant,

$$\begin{aligned} v \left(\frac{\partial p}{\partial T} \right)_v &= R \\ \left(\frac{\partial p}{\partial T} \right)_v &= \frac{R}{v} = \frac{p}{T} \\ \left(\frac{\partial u}{\partial v} \right)_T + p &= T \frac{p}{T} \\ \left(\frac{\partial u}{\partial v} \right)_T &= 0 \end{aligned}$$

Therefore, u does not change when v changes at constant temperature, when $u = (T, v)$

Similarly, if $u = (T, p)$, it can be shown that

$$\left(\frac{\partial u}{\partial p} \right)_T = 0$$

Therefore, u does not change with neither with p nor v when T is a constant.

That means, u does not change unless T changes.

That means, u is a function of T

$$u = f(T)$$

This is known as Joule's Law

If

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

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

Now, $\left(\frac{\partial u}{\partial v}\right)_T = 0$ and by definition, $c_v = \left(\frac{\partial u}{\partial T}\right)_v$

$$\therefore du = c_v dT$$

This equation holds good for an ideal gas for any process, whereas for any other substance, it is true for a constant volume process only.

Since c_v is constant for an ideal gas,

$$\Delta u = c_v \Delta T$$

The enthalpy of any substance is given by

$$h = u + pv$$

for an ideal gas,

$$pv = RT$$

$$h = u + RT$$

$$dh = du + R dT$$

Since R is a constant,

$$\Delta h = \Delta u + R \Delta T$$

$$\Delta h = c_v \Delta T + R \Delta T$$

$$\Delta h = (c_v + R) \Delta T$$

h is a function of T only and by definition,

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

$$dh = c_p dT$$

$$\Delta h = c_p \Delta T$$

$$c_p = c_v + R$$

The equation $dh = c_p dT$ holds good for an ideal gas, even when pressure changes, but for any other substance, this is true only for a constant pressure process.

Real Gas Relations

When the pressure is very small or temperature is very large, the intermolecular attraction and the volume of the molecules compared to the total volume of the gas are not of much significance, and the real gas obeys very closely the ideal gas equation.

But as pressure increases, the intermolecular forces of attraction and repulsion increase and also the volume of the molecules becomes appreciable compared to the total gas volume. Then the real gases deviate considerably from the ideal gas equation.

Van der Waals Equation

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

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

The coefficient “ a ” was introduced to account for the existence of mutual attraction between the molecules. The term “ a/v^2 ” is called the *force of cohesion*. The coefficient “ b ” was introduced to account for the volumes of the molecules and is known as *co-volume*.

Apart from van der Waals equation, three 2-constant equations of state are those of

Berthelot Equation:

$$p = \frac{RT}{v - b} - \frac{a}{Tv^2}$$

Dieterici Equation:

$$p = \left(\frac{RT}{v - b}\right) \cdot e^{\left(\frac{-a}{RTv}\right)}$$

Redlich-Kwong Equation:

$$p = \frac{RT}{v - b} - \frac{a}{T^{1/2}(v + b)}$$

The constants a and b are evaluated from the critical data for the gas.

Virial Expansion

The relation between $p\bar{v}$ and p in the form of power series is given below

$$p\bar{v} = (1 + B'p + C'p^2 + D'p^3 + \dots)$$

But for any gas,

$$\lim_{p \rightarrow 0} p\bar{v} = A = \bar{R}T$$

$$\bar{p}\bar{v} = \bar{R}T (1 + B'p + C'p^2 + D'p^3 + \dots)$$

$$\therefore \frac{p\bar{v}}{\bar{R}T} = 1 + B'p + C'p^2 + D'p^3 + \dots$$

Or,

$$\frac{p\bar{v}}{\bar{R}T} = 1 + B' \left(\frac{\bar{R}T}{\bar{v}} \right) + C' \left(\frac{\bar{R}T}{\bar{v}} \right)^2 + D' \left(\frac{\bar{R}T}{\bar{v}} \right)^3 + \dots$$

$$\frac{p\bar{v}}{\bar{R}T} = 1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \dots$$

These expressions are known as virial expansion or virial equations of state.

B' , C' , B , C etc. are known as virial coefficients.

B' & B are called the second virial coefficients

C' & C are called the third virial coefficients and so on.

For a given gas, these coefficients are functions of temperature only.

The ratio, $p\bar{v}/\bar{R}T$ is called the compressibility factor, Z

For an ideal gas, $Z = 1$

The magnitude of Z for a certain gas at a particular pressure and temperature gives an indication of the extent of deviation of the gas from the ideal gas behavior.

If the molecular attractions do not exist (at very low pressures), $B = 0$, $C = 0$, etc. $Z = 1$ and $p\bar{v} = \bar{R}T$

Compressibility Factor

The **compressibility factor (Z)**, also known as the **compression factor**, is the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. It is a useful thermodynamic property for modifying the ideal gas law to account for the real gas behavior. In general, deviation from ideal behavior becomes more significant the closer a gas is to a phase change, the lower the temperature or the larger the pressure

$$Z = \frac{p\bar{v}}{\bar{R}T}$$

Critical Temperature

Gases become more difficult to liquefy as the **temperature** increases because the kinetic energies of the particles that make up the gas also increase.

The **critical temperature** of a substance is the **temperature** at and above which vapor of the substance cannot be liquefied, no matter how much **pressure** is applied.

Critical Pressure

The **critical pressure** of a substance is the **pressure** at and above which liquid of the substance cannot be vaporized, no matter how much **heat** is applied.

Law of Corresponding States

According to van der Waals, the **theorem of corresponding states** (or **principle of corresponding states**) indicates that all fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from ideal gas behavior to about the same degree.

Compressibility Chart

For a certain gas,

- the compressibility factor Z is a function of p and T .
- A plot can be made of lines of constant temperature on coordinates of p and Z .
- From this plot Z can be obtained for any value of p and T ,
- Volume can then be obtained from the equation,

$$pv = ZRT$$

- The advantage of using Z instead of a direct plot of v is a smaller range of values in plotting.

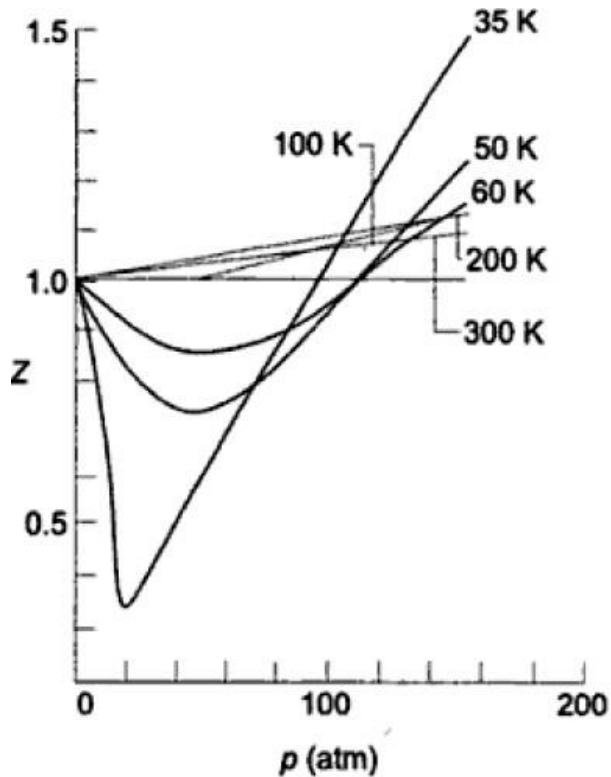


Figure 1 Compressibility chart for hydrogen

For each substance, there is a compressibility factor chart. If one chart could be used for all substances, it would be very convenient.

The general shapes of the vapor dome and of constant temperature lines on the $p - v$ plane are similar for all substances, although the scales may be different.

Generalized Compressibility Chart

By using dimensionless properties called reduced properties, it is possible to exploit the physical similarity between all substances.

- The reduced pressure is the ratio of the existing pressure to the critical pressure of the substance.

$$p_r = \frac{p}{p_c}$$

- The reduced temperature is the ratio of the existing temperature to the critical temperature of the substance.

$$T_r = \frac{T}{T_c}$$

- The reduced volume is the ratio of the existing volume to the critical volume of the substance.

$$v_r = \frac{v}{v_c}$$

Where the subscript r denotes reduced property and subscript c denotes the property at the critical state.

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

Therefore, for all substance,

$$v_r = f(p_r, T_r)$$

Now,

$$v_r = \frac{v}{v_c} = \left[\frac{\left(\frac{ZRT}{p}\right)}{\left(\frac{Z_c RT_c}{p_c}\right)} \right] = \frac{Z}{Z_c} \times \frac{T_r}{p_r}$$

Where, the critical compressibility factor,

$$Z_c = \frac{p_c v_c}{RT_c}$$

Therefore,

$$Z = \frac{v_r Z_c p_r}{T_r} = \frac{f(p_r, T_r) Z_c p_r}{T_r} = f(p_r, T_r, Z_c)$$

Experimental values of Z_c for most substances fall within a narrow range 0.20 – 0.30. Therefore, Z_c may be taken to be a constant.

$$\therefore Z = f(p_r, T_r)$$

When T_r is plotted as a function of reduced pressure and Z , a single plot known as the “generalized compressibility chart” is found to be satisfactory for a great variety of substances.

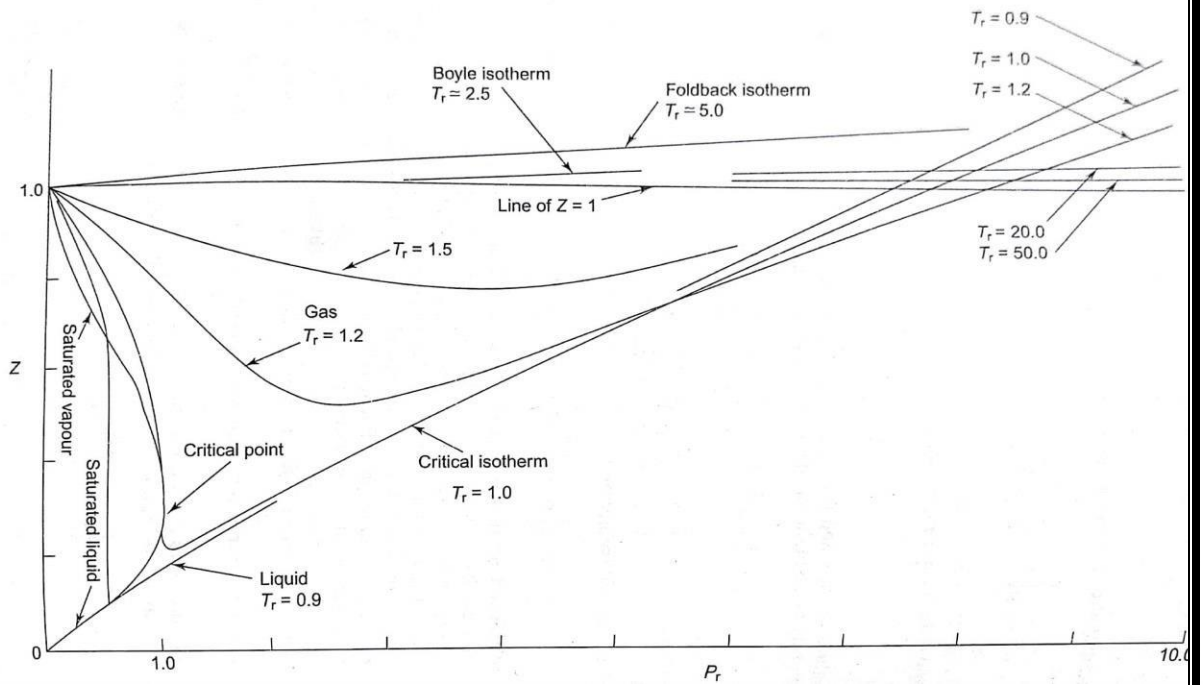
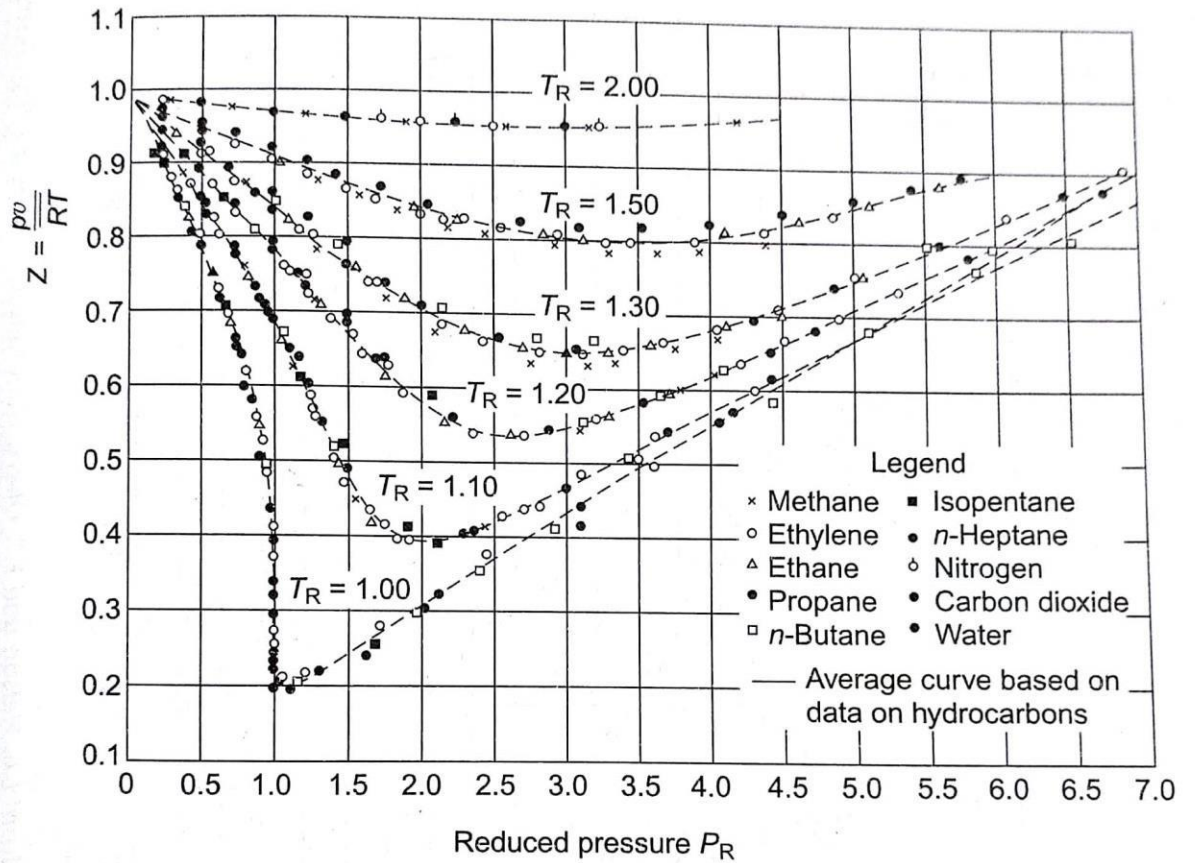


Figure 2 Generalized compressibility chart



MODULE V

Mixture of ideal gases

Mole Fraction

Mole fraction is another way of expressing the concentration of a solution or mixture. It is equal to the moles of one component divided by the total moles in the solution or mixture.

Mole Fraction or Molar Fraction,

$$x_i = \frac{n_i}{n_{total}}$$

$$\sum_{i=1}^N n_i = n_{total}$$

The sum of all mole fractions is equal to 1

$$\sum_{i=1}^N x_i = 1$$

Mass Fraction

Mass fraction of a gas in a gas mixture is defined as the ratio between the mass of the gas and the total mass of the gas mixture.

$$y_i = \frac{m_i}{m_{total}}$$

Now, Number of Moles,

$$n_i = \frac{m_i}{\mu_i}$$

m = Mass (kg)

μ = Molecular Weight

$$\therefore m_i = n_i \times \mu_i$$

For the gas mixture,

$$\mu = \frac{m}{n} = \frac{\sum_{i=1}^N m_i}{\sum_{i=1}^N n_i} = \frac{\sum_{i=1}^N n_i \mu_i}{\sum_{i=1}^N n_i} = \frac{n_1 \mu_1}{n_{total}} + \frac{n_2 \mu_2}{n_{total}} + \frac{n_3 \mu_3}{n_{total}} + \dots$$

$$\mu = x_1 \mu_1 + x_2 \mu_2 + x_3 \mu_3 + \dots$$

$$\therefore \mu = \sum_{i=1}^N x_i \mu_i$$

Gravimetric Analysis

If the composition of a mixture is described by specifying the mass of each component, then it is called as gravimetric analysis.

Molar analysis

If the number of moles of each component is specified, then it is called as molar analysis.

Volumetric analysis

If the volume of each component is specified, then it is called as volumetric analysis

Dalton's Law of Partial Pressures

Imagine a homogeneous mixture of inert ideal gases at a temperature T , a pressure p and volume V . Let us suppose there are n_1 moles of a gas A_1 , n_2 moles of gas A_2 , ... and up to n_c moles of gas A_c .

Since there is no chemical reaction, the mixture is in a state of equilibrium with the equation of state.

$$pV = n\bar{RT}$$
$$pV = (n_1 + n_2 + \dots + n_c)(\bar{RT})$$
$$p = \frac{(n_1 + n_2 + \dots + n_c)\bar{RT}}{V}$$
$$p = \frac{n_1\bar{RT}}{V} + \frac{n_2\bar{RT}}{V} + \frac{n_3\bar{RT}}{V} + \dots$$
$$\frac{n_1\bar{RT}}{V} = p_1; \frac{n_2\bar{RT}}{V} = p_2; \dots$$

p_1, p_2, p_3 are known as the partial pressures.

$$p = p_1 + p_2 + p_3 + \dots$$

Therefore, the total pressure of a mixture of ideal gases is equal to the sum of the partial pressures

This is known as Dalton's law of partial pressures.

$$V = (n_1 + n_2 + \dots + n_c) \frac{\bar{RT}}{p}$$

$$V = \sum n_k \frac{\bar{RT}}{p}$$

And the partial pressure for the K th gas is

$$\begin{aligned}
 p_K &= \frac{n_K \bar{RT}}{V} \\
 &= \frac{n_K \bar{RT}}{\sum n_K \frac{RT}{p}} \\
 &= \frac{n_K p}{\sum n_K} \\
 p_K &= \frac{n_K}{\sum n_K} p
 \end{aligned}$$

$$\sum n_K = n_1 + n_2 + n_3 + \dots + n_c$$

$\sum n_K =$ Total Number of moles of a gas

The ratio $\frac{n_K}{\sum n_K}$ is called mole fraction of the K th gas, and is denoted by x_K

Thus,

$$x_1 = \frac{n_1}{\sum n_K}; x_2 = \frac{n_2}{\sum n_K}; \dots$$

And

$$p_1 = x_1 p; p_2 = x_2 p; p_3 = x_3 p; \text{ etc.}$$

$$p_K = x_K p$$

Also,

$$x_1 + x_2 + x_3 + \dots + x_c = 1$$

Amagat's law of additive volumes

Partial volume of a component of a mixture is the volume that the component alone would occupy at the pressure and temperature of the mixture.

$$pV_1 = m_1 R_1 T; pV_2 = m_2 R_2 T; \dots pV_c = m_c R_c T$$

Or

$$(V_1 + V_2 + V_3 + \dots + V_c) = (m_1 R_1 + m_2 R_2 + m_3 R_3 + \dots + m_c R_c) T$$

$$\text{Now, } pV = (m_1 R_1 + m_2 R_2 + m_3 R_3 + \dots + m_c R_c) T$$

$$\text{And, } pV = (m_1 + m_2 + m_3 + \dots + m_c) R_m T$$

$$\therefore \boxed{V = V_1 + V_2 + V_3 + \dots + V_c}$$

The total volume is thus equal to the sum of the partial volumes. *This is known as Amagat's law of additive volumes.*

The specific volume of the mixture, v is given by

$$v = \frac{V}{m} = \frac{V}{m_1 + m_2 + m_3 + \dots + m_c}$$

$$\frac{1}{v} = \frac{m_1 + m_2 + m_3 + \dots + m_c}{V} = \frac{m_1}{V} + \frac{m_2}{V} + \frac{m_3}{V} + \dots + \frac{m_c}{V}$$

$$\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2} + \frac{1}{v_3} + \dots + \frac{1}{v_c}$$

Density of the mixture,

$$\rho = \rho_1 + \rho_2 + \rho_3 + \dots + \rho_c$$

Equivalent gas constant and molecular weight

The total mass of the gas mixture,

$$m = (m_1 + m_2 + m_3 + \dots + m_c)$$

Again, in terms of the masses,

$$p_1V = m_1R_1T$$

$$p_2V = m_2R_2T$$

.....
.....

$$p_cV = m_cR_cT$$

Using Dalton's Law,

$$pV = (m_1R_1 + m_2R_2 + m_3R_3 + \dots + m_cR_c)$$

Where $p = p_1 + p_2 + p_3 + \dots + p_c$

For the gas mixture,

$$pV = (m_1 + m_2 + m_3 + \dots + m_c)$$

R_m is the equivalent gas constant for the mixture,

$$\therefore R_m = \frac{(m_1R_1 + m_2R_2 + m_3R_3 + \dots + m_cR_c)}{(m_1 + m_2 + m_3 + \dots + m_c)}$$

The gas constant is thus the weighted mean, on a mass basis, of the gas constants of the components.

If μ denotes the equivalent molecular weight of the mixture having n total number of moles,

$$n\mu = n_1\mu_1 + n_2\mu_2 + \dots + n_c\mu_c$$

$$\mu = \frac{n_1\mu_1 + n_2\mu_2 + \dots + n_c\mu_c}{n} = x_1\mu_1 + x_2\mu_2 + \dots + x_c\mu_c$$

$$\mu = x_K\mu_K$$

Molecular weight of air with 21% O₂, 78% N₂, 1% Ar

$$\begin{aligned}\mu_{air} &= 0.78 \times 28 + 0.21 \times 32 + 0.01 \times 40 \\ &= 21.84 + 6.72 + 0.4 = 28.96\end{aligned}$$

Properties of gas mixtures:

Internal Energy (Gibbs Dalton's Law)

The internal energy of a mixture of gases is equal to the sum of the internal energies of the individual component, each taken at the temperature and volume of the mixture (i.e. sum of the partial internal energies).

This is also true for any of the thermodynamic properties and is known as Gibbs Theorem.

$$mu_m = m_1u_1 + m_2u_2 + m_3u_3 + \dots + m_cu_c$$

The average internal energy of the mixture,

$$u_m = \frac{m_1u_1 + m_2u_2 + m_3u_3 + \dots + m_cu_c}{m_1 + m_2 + m_3 + \dots + m_c}$$

Enthalpy

The total enthalpy of the gas mixture is the sum of the partial enthalpies.

$$mh_m = m_1h_1 + m_2h_2 + m_3h_3 + \dots + m_ch_c$$

The average enthalpy of the mixture,

$$h_m = \frac{m_1h_1 + m_2h_2 + m_3h_3 + \dots + m_ch_c}{m_1 + m_2 + m_3 + \dots + m_c}$$

Specific Heats

$$c_{v_m} = \frac{m_1c_{v_1} + m_2c_{v_2} + m_3c_{v_3} + \dots + m_cc_{v_c}}{m_1 + m_2 + m_3 + \dots + m_c}$$

$$c_{p_m} = \frac{m_1c_{p_1} + m_2c_{p_2} + m_3c_{p_3} + \dots + m_cc_{p_c}}{m_1 + m_2 + m_3 + \dots + m_c}$$

Entropy

Gibbs theorem states that the total entropy of a mixture of gases is the sum of the partial entropies.

The partial entropy of one of the gases of a mixture is the entropy that the gas would have if it occupied the whole volume alone at the same temperature.

A change in entropy due to the diffusion of any number of inert ideal gases is,

$$S_f - S_i = -R \left(n_1 \ln \frac{p_1}{p} + n_2 \ln \frac{p_2}{p} + \dots + n_c \ln \frac{p_c}{p} \right)$$

Which indicates that each gas undergoes in the diffusion process a free expansion from the total pressure p to the respective partial pressure at constant temperature.

$$\begin{aligned} S_f - S_i &= - \sum m_K R_K \ln \left(\frac{p_K}{p} \right) \\ &= - [m_1 R_1 \ln \left(\frac{p_1}{p} \right) + m_2 R_2 \ln \left(\frac{p_2}{p} \right) + \dots + m_c R_c \ln \left(\frac{p_c}{p} \right)] \end{aligned}$$

Kay's Rule

Proposed by W. B. Kay in 1963

A mixture is treated pseudo pure substance

Pseudo Critical pressure,

$$\begin{aligned} p'_{cr} &= \sum_{i=1}^k x_i p_{cr,i} \\ p_R &= \frac{p}{p_{cr}} \end{aligned}$$

$p_{cr,i}$, is the critical pressure of each component in the mixture

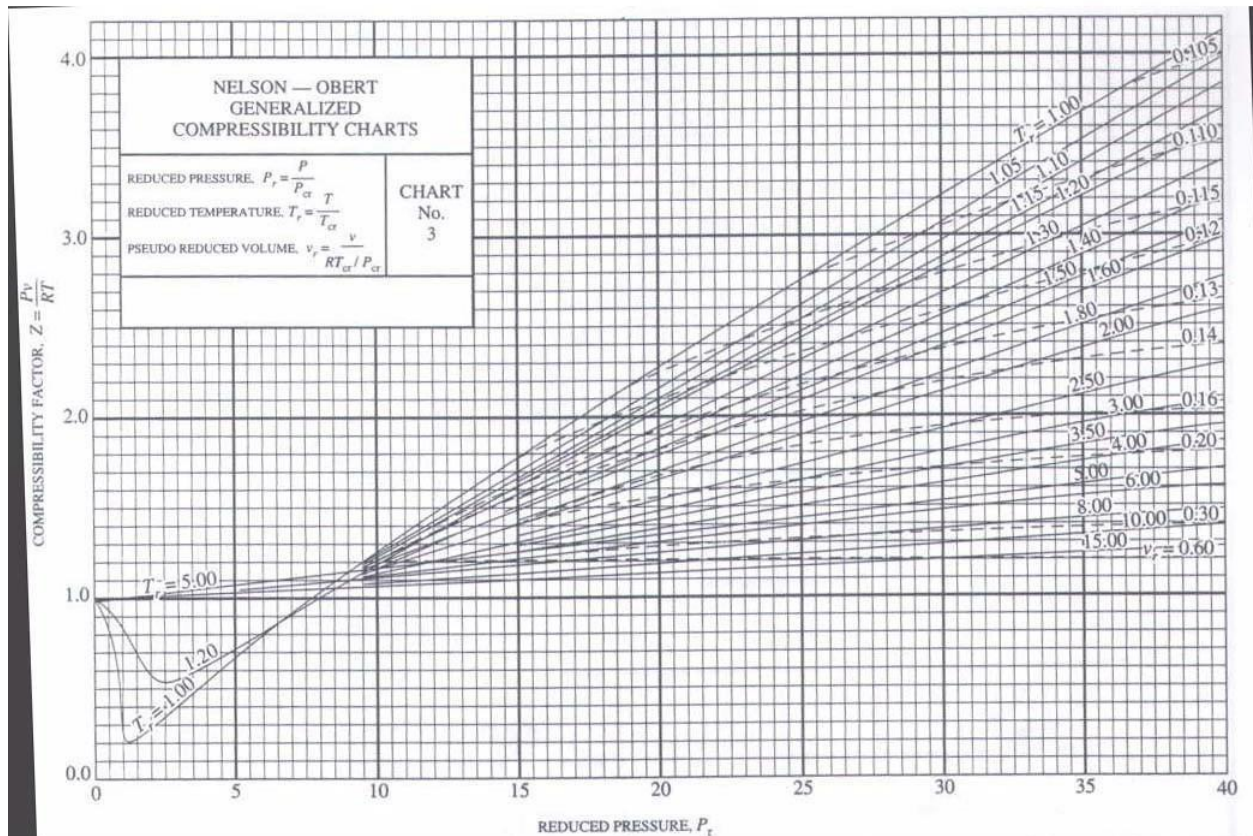
x_i , Mole Fraction

Pseudo Critical Temperature,

$$\begin{aligned} T'_{cr} &= \sum_{i=1}^k x_i T_{cr,i} \\ T_R &= \frac{T}{T'_{cr}} \end{aligned}$$

The compressibility factor is determined using Nelson Obert Generalized Compressibility Chart for the reduced pressure and reduced temperature.

Nelson-Obert Generalized (Averaged) Compressibility Chart



The results obtained using Kay's Rule is accurate to within 10% over a wide range of temperatures and pressures.

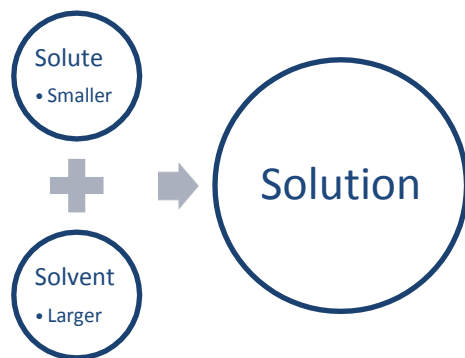
Introduction to Ideal Binary Solutions

Definition of Solution

- A system with more than one chemical component that is homogeneously mixed at the molecular level.
- Homogeneous mixture of two or more than two substances (components) such that its properties and composition are uniform throughout the mixture

Composition of Solution

- Solute - Constitutes the smaller part of the solution
- Solvent - Constitutes the larger part of the solution



Binary Solutions

- A solution of two substances is called as a binary solution.
- The component which is present in small amount is called solute and the other component is called solvent.

Characteristics

- Composed of only one phase
- The solute from the solution cannot be separated by filtration
- The particles of solute in a solution cannot be seen through naked eye
- Solution does not allow the light to scatter.

Types of Binary Solutions

Type	Solute	Solvent	Example
Gaseous	Gas	Gas	O ₂ & N ₂ gas
	Liquid	Gas	Chloroform with N ₂
	Solid	Gas	Camphor in N ₂
Liquid	Gas	Liquid	O ₂ in H ₂ O
	Liquid	Liquid	Ethanol in H ₂ O
	Solid	Liquid	Glucose in H ₂ O
Solid	Gas	Solid	H ₂ in Palladium
	Liquid	Solid	Amalgum of Mercury with Sodium
	Solid	Solid	Copper in Gold

Homogenous Uniform Composition

Heterogenous Non uniform

Composition^{Aqueous} Water is the

solvent

Non-Aqueous Water is not the solvent

Dilute Less amount of solute

Concentrated More amount of solute

Methods of Expressing Concentration

Mass Percentage

$$\text{Mass \%} = \frac{\text{Mass of the component}}{\text{Total mass of the solution}} \times 100$$

Volume Percentage

$$\text{Volume \%} = \frac{\text{Volume of component}}{\text{Total volume of the solution}} \times 100$$

Mole Fraction

$$M = \frac{\text{No. of moles of solute}}{\text{No. of moles of solution}}$$

Molarity

$$M = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

Molality

$$m = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Normality

$$N = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in litres}}$$

$$\text{No. of gram equivalent} = \frac{\text{mass of solute}}{\text{equivalent weight of solute}}$$

Parts per million

$$\text{ppm} = \frac{\text{Mass (or volume) of solute}}{\text{Total mass (or volume) of solution}} \times 10^6$$

1PPM = 1MG/LITRE

Solubility

Solubility of a substance is defined as the maximum amount of solute that can be dissolved in a given amount of solvent at a constant temperature.

It is expressed as mol/lit.

$$\text{Solubility} = \frac{\text{Amount of substance (solute) dissolved}}{\text{Amount of solvent}} \times 100$$

Vapor Pressure

If a liquid is partially filled and sealed in a container then, any molecules which escapes from the surface of the liquid will be contained in the evacuated space above the liquid and thus exert a pressure on the container.

As more molecules enter the space, the possibility of re-entering molecules also increases.

Thus a state of dynamic equilibrium exists, where as many particles which are leaving are entering are returning. The pressure exerted on the liquid at this state is known as saturated vapor pressure.

Raoult's Law

When a substance is dissolved in a solution, the vapor pressure of the solution decreases.

For a solution of volatile liquids, the partial vapor pressure of each component of the solution is directly proportional to its mole fraction present in the solution.

Raoult's Law states that the partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapour pressure of the pure component multiplied by its mole fraction in the mixture.

Mathematically, Raoult's law for a single component in an ideal solution is stated as

$$p_i = x_i p_i^*$$

p_i is the partial pressure of the component i in the mixture.

p_i^* is the vapor pressure of the pure component i in the mixture at the same temperature.

x_i is the mole fraction of component i in the mixture.

Once the components in the solution have reached equilibrium, the total vapor pressure of the solution can be determined by combining Raoult's law with Dalton's law of partial pressures to give.

$$p = x_1 p_1^* + x_2 p_2^* + \dots + x_c p_c^*$$

Vapor pressure of liquid – liquid solution

p_{total} = Total Vapor Pressure

p_1 = Partial pressure of component 1

p_2 = Partial pressure of component 2

x_1 = Mole Fraction of component 1

x_2 = Mole Fraction of component 2

From Dalton's Law,

$$p_{total} = p_1 + p_2$$

$$p_i = x_i p_i^*$$

p_i^* is the vapor pressure of the pure component at the same temperature.

$$p_1 = p_1^* x_1$$

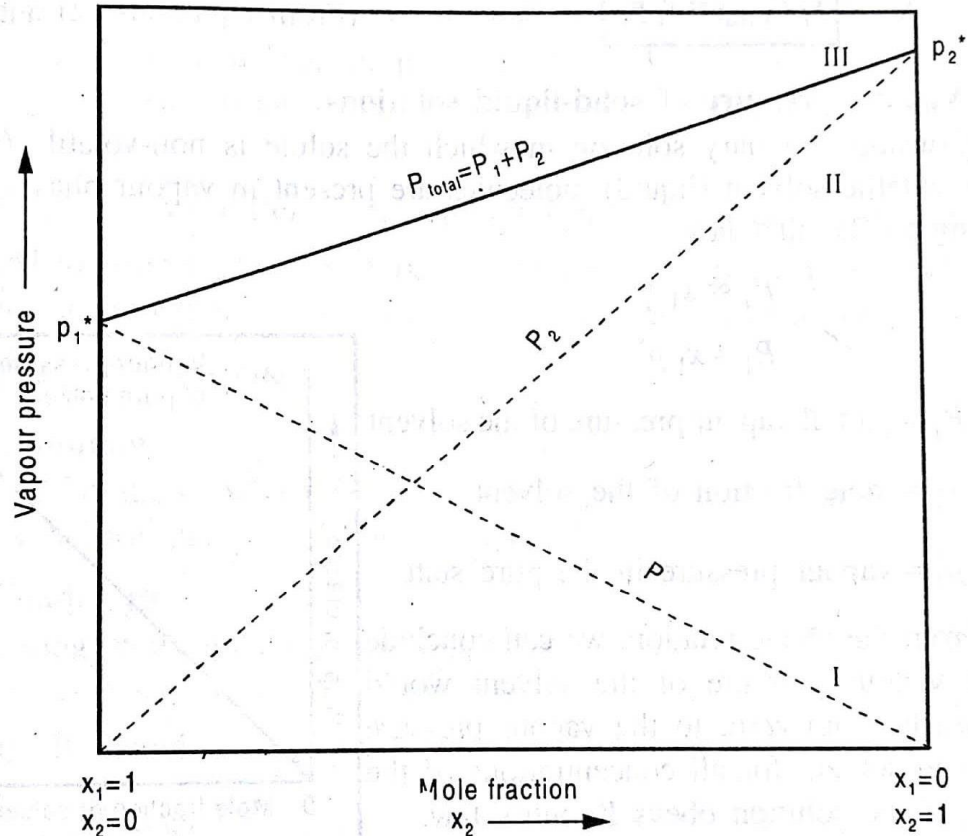
$$p_2 = p_2^* x_2$$

$$\therefore p_{total} = x_1 p_1^* + x_2 p_2^*$$

$$= (1 - x_2) p_1^* + x_2 p_2^*$$

$$p_{solution} = p_{total} = p_1^* + (p_2^* - p_1^*) x_2$$

- Total vapor pressure over the solution can be found out using the mole fraction of any one component
- Total vapor pressure over the solution varies linearly with the mole fraction of the component
- Depending on the vapor pressures of the pure components 1 and 2, the total vapor pressure over the solution decreases or increases with the increase of the mole fraction of the component.



A plot of vapor pressure and mole fraction for an ideal solution gives a linear plot as shown in the figure.

The dashed lines I and II represents the partial pressure of the components.

The line III represents the total vapor pressure line which varies linearly with x_2

Assuming component 1 is less volatile than component 2, i.e. $p_1^* < p_2^*$

The minimum value of p_{total} is p_1^* and the maximum value of p_{total} is p_2^*

If the component is in vapor phase, then

$$p_1 = p_{total}y_1$$

$$p_2 = p_{total}y_2$$

Where y_1 and y_2 are the mole fractions of the components in the vapor phase.

$$y_i p_{total} = x_i p_i^*$$

Therefore,

1. Vapour phase is an ideal gas
2. Liquid phase is an ideal solution.

Vapor pressure of solid-liquid solutions

Consider a binary solution in which the solute is non-volatile and the volatile solvent molecules are present in vapor phase,

Then according to Raoult's Law,

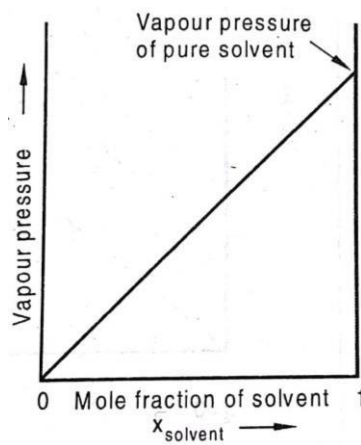
$$p_1 \propto x_1$$

$$p_1 = x_1 p_1^*$$

p_1 = Partial Vapor Pressure of the solvent

x_1 = Mole fraction of the solvent

p_1^* = Vapor pressure in the pure state



Ideal Solutions

Solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions

During the formation of ideal solutions, no change in enthalpy or volume takes place

Practically, there is no solution which behaves as the ideal solution. Only very dilute solutions behave as ideal solutions.

Characteristics

- The volume of the solution varies linearly with composition
- Heat is neither absorbed nor released while mixing the liquids
- The total vapor pressure of the solution varies linearly with composition

- The average intermolecular forces of attraction and repulsion in the solution remains unchanged on mixing the pure liquids.

Deviation from Ideality

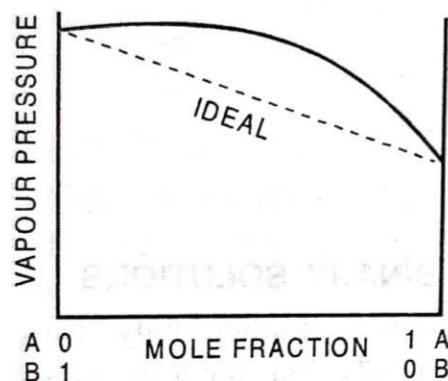
The solutions which does not obey Raoult's Law over the entire range of concentration are known as non-ideal solution

For non-ideal solutions,

1. Raoult's law is not obeyed
2. $\Delta H_{mixture} \neq 0$
3. $\Delta V_{mixture} \neq 0$

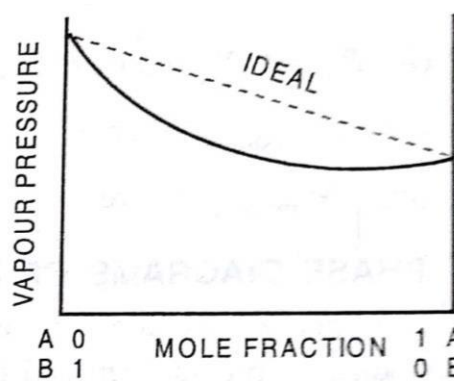
The non-ideal solutions are further classified into two categories

- I. Solutions with positive deviation
- II. Solutions with negative deviation



POSITIVE DEVIATION

(a). Vapour pressure is greater than ideal



NEGATIVE DEVIATION

(b). Vapour pressure is less than ideal

Solutions with Positive Deviation

- i. Solution in which solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions
- ii. At intermediate composition, the vapour pressure of the solution is maximum
- iii. At intermediate composition, the boiling point is minimum.

Solutions with Negative Deviation

- i. Solution in which solvent-solvent and solute-solute interactions are weaker than solute-solvent interactions.

- ii. At intermediate composition, the vapor pressure of the solution is minimum
- iii. At intermediate composition, the boiling point is maximum

Phase Diagram

For a binary solution, the Gibb's phase rule gives

$$F = C - P + 2$$

C – No. of components

P – Phase

F – Degree of Freedom

Pressure – Composition Phase Diagram

- The temperature is kept constant.
- Mole fraction of one component is plotted on the horizontal axis.
- Pressure is plotted on the vertical axis.

For a two-component solution,

$$p_{total} = p_1 + p_2 = x_1 p_1^* + x_2 p_2^*$$

$$p_{total} = p_1^* + (p_2^* - p_1^*) x_2$$

Where, $x_1 = (1 - x_2)$

The composition of the vapor phase at equilibrium with a liquid solution is not the same as the liquid solution itself.

If an ideal gas mixture is at equilibrium with a 2-component ideal solution, the mole fraction of component 1 in the gaseous phase is given by Dalton's Law

$$p_1 = p_{total} \times y_1$$

$$\therefore y_1 = \frac{p_1}{p_{total}} = \frac{x_1 p_1^*}{p_1^* + (p_2^* - p_1^*) x_2}$$

Similarly, to find the mole fraction in the liquid phase,

$$y_1 p_{total} = x_1 p_1^*$$

$$x_1 = \frac{y_1 p_{total}}{p_1^*}$$

$$x_2 = \frac{y_2 p_{total}}{p_2^*}$$

$$\therefore p_{total} = p_1^* + (p_2^* - p_1^*) x_2 \rightarrow f(x_2)$$

$$p_{total} = p_1^* + (p_2^* - p_1^*) \frac{y_2 p_{total}}{p_2^*}$$

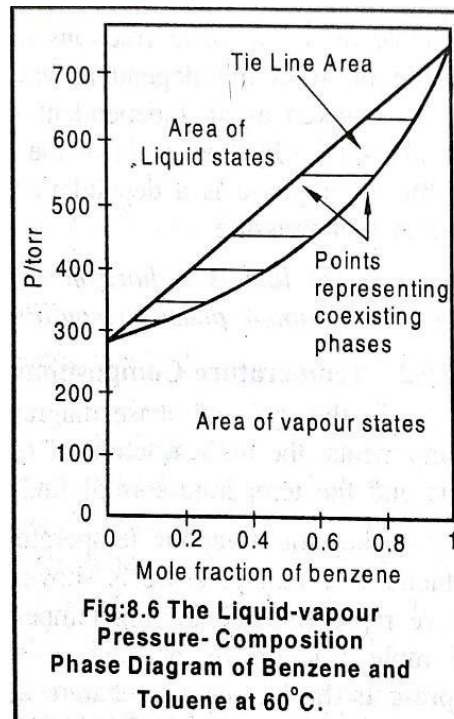
$$p_2^* p_{total} = p_1^* p_2^* + y_2 p_2^* p_{total} - y_2 p_1^* p_{total}$$

$$p_2^* p_{total} - y_2 p_2^* p_{total} + y_2 p_1^* p_{total} = p_1^* p_2^*$$

$$p_t (p_2^* - y_2 p_2^* + y_2 p_1^*) = p_1^* p_2^*$$

$$p_{total} = \frac{p_1^* p_2^*}{p_2^* - y_2 p_2^* + y_2 p_1^*}$$

$$p_{total} = \frac{p_1^* p_2^*}{p_2^* + y_2 (p_1^* - p_2^*)} \rightarrow ()_2$$



- The lower curve represents the total pressure as a function of the mole fraction of the vapor phase at equilibrium with the liquid phase. The area below this curve represent possible equilibrium states of the system when it is a one phase vapor.
- The upper curve represents the total pressure as a function of the mole fraction in the liquid. The area above this line represents the equilibrium states of the system when it is one phase liquid.
- At a given pressure, the horizontal line segments connect the state points between the two curves for phases at equilibrium with each other and are called TIE LINES.

- If the pressure is taken as an independent variable, then the mole fractions in the two phases, represented by the ends of the tie lines are dependent variables.
- If the mole fraction of one phase is taken as an independent variable, then the pressure is a dependent variable given by the height of the curve for that phase and the mole fraction of the other phase is a dependent variable given by the other end of the tie line at that pressure.

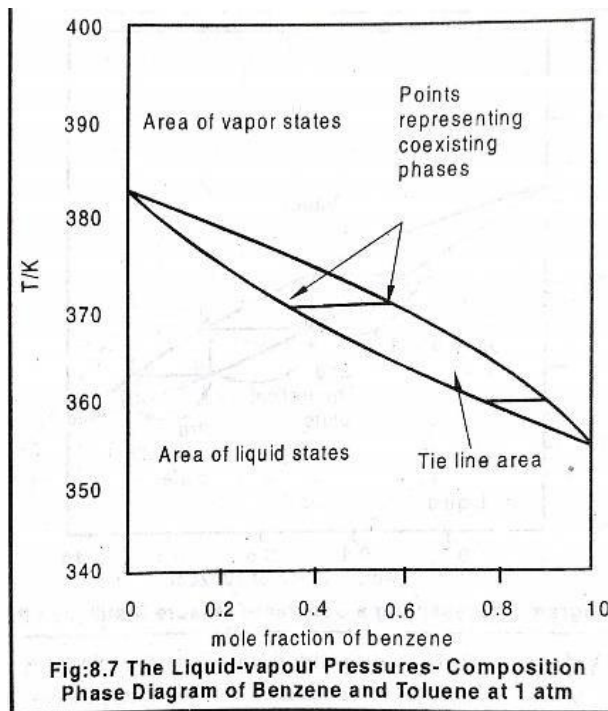
Temperature – Composition Phase Diagram

In this type of phase diagram, the pressure is held constant.

The temperature composition phase diagram is drawn with the temperature on the vertical axis and the mole fraction on the horizontal axis.

The tie lines which is drawn between the two curves, connect the values of the mole fraction in the two phases at equilibrium with each other.

The tie line should be the same as that drawn on the pressure – composition phase diagram.

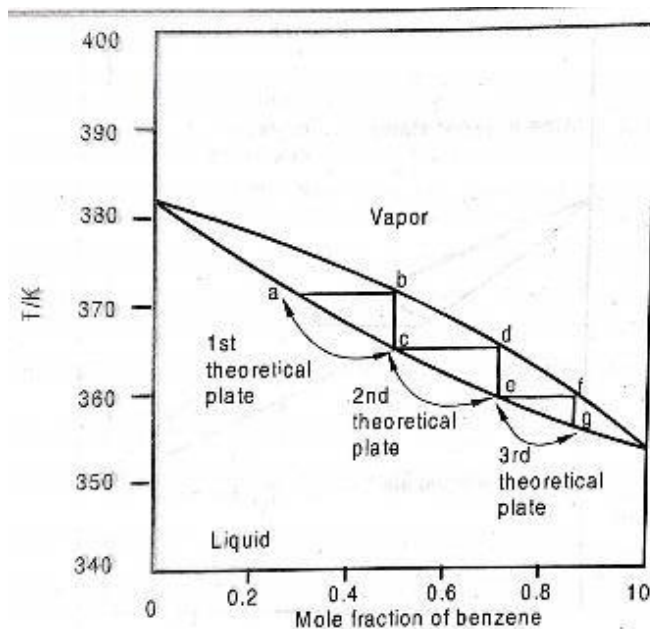


Distillation Process

A constant pressure distillation process can be described by using the temperature composition phase diagram.

The process is carried out by means of a simple still used in distilling spirits, liquids etc.

A separation of the components of the solution is done by packing a column with glass beads or other objects. The liquid that moves up that column condenses on the glass bead, moves up the column and then evaporates again. That part of the column where the vapor condenses is equivalent to one “theoretical plate”. *A theoretical plate in many separation processes is a hypothetical zone or stage in which two phases, such as the liquid and vapor phases of a substance, establish an equilibrium with each other.*



In the figure,

- Point ‘a’ represents the composition of liquid solution that is being boiled.
- Point ‘b’ represents the composition of the vapor at the other end of the tie line which is in equilibrium with the liquid phase.
- Point ‘c’ on the diagram represents the temperature at which the vapor condenses.
- Thus the process from ‘a’ to ‘c’ corresponds to one theoretical plate.

A second vaporization – condensation cycle starts at point ‘c’ which leads to a vapor with composition at point ‘d’ and this vapor can condense further up the column corresponding to point ‘e’.

Hence this process from ‘c’ to ‘e’ corresponds to the next theoretical plate.

Process ‘a’ to ‘e’ corresponds to two theoretical plates.

Lever Rule

The lever rule is a tool used to determine the mole fraction of each phase of a binary equilibrium phase diagram. It is used to determine the percent of liquid and solid phases for a given binary composition and temperature that is between the liquidus and solidus line.

Before any calculations can be made, a tie line is drawn on the phase diagram to determine the percentage weight of each element; on the phase diagram to the right it is line segment LS. This tie line is drawn horizontally at the composition's temperature from one phase to another (here the liquid to the solid). The percent weight of element B at the liquidus is given by W_L and the percent weight of element B at the solidus is given by W_S . The percent weight of solid and liquid can then be calculated using the following lever rule equations:

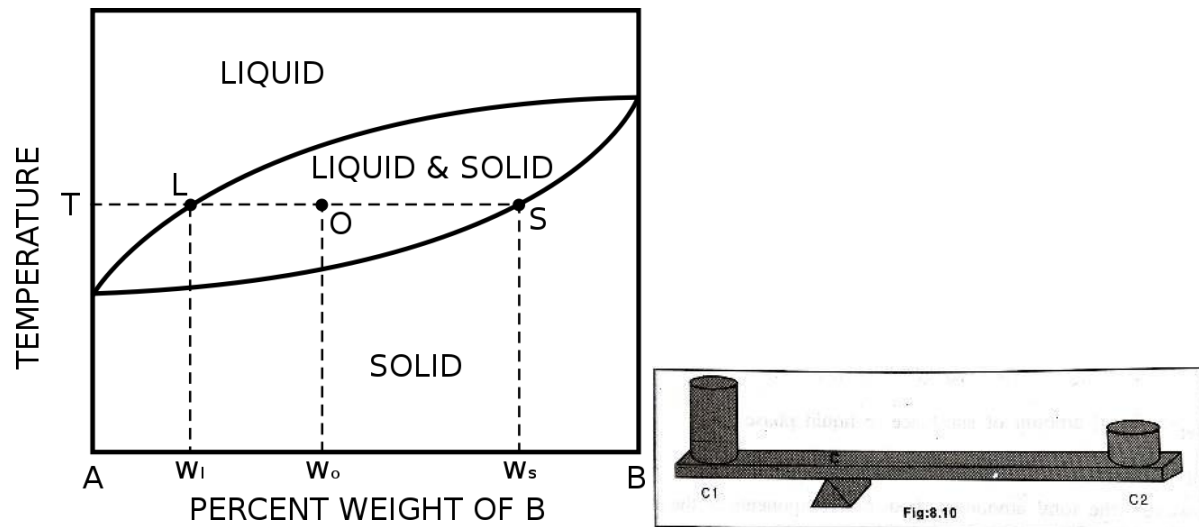
Percent Weight of the Solid Phase

$$X_s = \frac{W_o - W_L}{W_S - W_L}$$

Percent Weight of the Liquid Phase

$$X_L = \frac{W_S - W_o}{W_S - W_L}$$

where W_o is the percent weight of element B for the given composition.



Thermodynamic Relations

Mathematical Theorems

Theorem 1

Some relation exists between x, y, z

$$dz = \left(\frac{\partial z}{\partial y}\right)_x dy + \left(\frac{\partial z}{\partial x}\right)_y dx$$

Now, let

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

$$\therefore dz = Mdy + Ndx$$

Hence,

$$\left(\frac{\partial M}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

And

$$\left(\frac{\partial N}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y}$$

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

This is the condition for exact or perfect differential.

Theorem 2

If a quantity f is a function of x, y and z and a relation exists among x, y and z , then f is a function of any two of x, y and z .

Similarly, any one of x, y and z may be regarded to be a function of f and any one of x, y and z . Thus if

$$x = x(f, y)$$
$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy$$

And if

$$y = y(f, z)$$

$$dy = \left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz$$

Substituting for dy is the previous relation, we get

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f \left[\left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz\right]$$

$$\therefore dx = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z\right] df + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f dz$$

Also,

$$x = x(f, z)$$

$$\Rightarrow dx = \left(\frac{\partial x}{\partial f}\right)_z df + \left(\frac{\partial x}{\partial z}\right)_f dz$$

Comparing the coefficients of dz , we get

$$\left(\frac{\partial x}{\partial z}\right)_f = \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f$$

$$\therefore \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$$

Theorem 3

Among the variables x , y and z , any one variable may be considered as a function of the other two.

$$x = x(y, z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Similarly,

$$z = z(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Substituting the value of dz , we get

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\right]$$

$$dx = \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right] dy + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y dx$$

$$dx = \left[\left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \right] dy + dx$$

$$\left[\left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \right] dy = 0$$

$$\left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x$$

$$\therefore \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

Among the thermodynamic variables p , V and T , the following relation holds good.

$$\left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_V = -1$$

Helmholtz's Function

$$F = U - TS$$

Significance

The work done by a system in any process between two equilibrium states at the same temperature during which the system exchanges heat only with the environment is equal to or less than the decrease in the Helmholtz function of the system during the process.

Gibb's Function

$$G = H - TS$$

Significance

The decrease in the Gibbs functions of a system sets an upper limit to the work that can be performed, exclusive of pdV work, in any process between two equilibrium states at the same temperature and pressure, provided the system exchanges heat only with the environment which is at the same temperature and pressure as the end states of the system.

Maxwell's Relations

The eight thermodynamic properties viz.

1. p (Pressure)
2. V (Volume)
3. T (Temperature)
4. S (Entropy)
5. U (Internal Energy)
6. H (Enthalpy $H = U + pV$)
7. F (Helmholtz's Function $F = U - TS$)
8. G (Gibb's Function $G = H - TS$)

Out of these eight, any one may be expressed as a function of any two others.

$$dQ = dU + pdV$$

$$\therefore dU = TdS - pdV \quad \text{-----(1)}$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$\therefore dH = TdS + Vdp \quad \text{-----(2)}$$

$$F = U - TS$$

$$dF = dU - (TdS + SdT)$$

$$\therefore dF = -pdV - SdT \quad \text{-----(3)}$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = TdS + Vdp - TdS - SdT$$

$$\therefore dG = Vdp - SdT \quad \text{-----(4)}$$

Equations (1), (2), (3) and (4) are all of the form

$$dz = Mdx + Ndy$$

and, from Theorem 1,

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

\therefore from (1), we have

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V}$$

and from (2), we have

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

from (3), we have

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

from (4), we have

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial P}\right)_T$$

These four equations are called as the Maxwell's Relations

TdS Equations

Let the entropy S be imagined to be a function of T and V . Then

$$\begin{aligned} S &= S(T, V) \\ dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ \therefore TdS &= T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV \end{aligned}$$

Now, heat transferred during a constant volume process,

$$\begin{aligned} dQ &= TdS = C_v dT \\ \therefore C_v &= \frac{TdS}{dT} = T \left(\frac{\partial S}{\partial T}\right)_V \end{aligned}$$

Also, from Maxwell's third equation,

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\therefore TdS = C_v dT + T \left(\frac{\partial p}{\partial T}\right)_V dV$$

This is known as the *first TdS* equation.

If, $S = (T, p)$,

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \\ TdS &= T \left(\frac{\partial S}{\partial T}\right)_p dT + T \left(\frac{\partial S}{\partial p}\right)_T dp \end{aligned}$$

$$T \left(\frac{\partial S}{\partial T} \right)_p = \text{and} \quad \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$$

Then,

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp$$

This is known as the *second TdS* equation

Equation of Specific Heats

Equating the first and second *TdS* equations, we get

$$\begin{aligned} TdS &= C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dV = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \\ C_p dT - C_v dT &= T \left(\frac{\partial p}{\partial T} \right)_v dV + T \left(\frac{\partial V}{\partial T} \right)_p dp \\ dT &= \frac{T \left(\frac{\partial p}{\partial T} \right)_v dV + T \left(\frac{\partial V}{\partial T} \right)_p dp}{C_p - C_v} = \frac{T \left(\frac{\partial p}{\partial T} \right)_v}{C_p - C_v} dV + \frac{T \left(\frac{\partial V}{\partial T} \right)_p}{C_p - C_v} dp \end{aligned}$$

Temperature T can be assumed to be a function of volume V and pressure p

$$\begin{aligned} T &= T(V, p) \\ dT &= \left(\frac{\partial T}{\partial V} \right)_p dV + \left(\frac{\partial T}{\partial p} \right)_v dp \end{aligned}$$

Now equating the terms of dV and dp in both the preceding equations, we get

$$\left(\frac{\partial T}{\partial V} \right)_p = \frac{T \left(\frac{\partial p}{\partial T} \right)_v}{C_p - C_v}$$

And

$$\left(\frac{\partial T}{\partial p} \right)_v = \frac{T \left(\frac{\partial V}{\partial T} \right)_p}{C_p - C_v}$$

Both these equations give,

$$C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p$$

But,

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1$$

$$\therefore \left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p - C_v = T \left[-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \right] \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p - C_v = -T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p^2$$

In this equation,

The term, $\left(\frac{\partial V}{\partial T}\right)_p^2$ is always positive.

The term $\left(\frac{\partial p}{\partial V}\right)_T$ is always negative, since p is $\propto \frac{1}{V}$ (Boyle's Law)

Therefore, $C_p - C_v$ is always positive.

That is, $C_p > C_v$

As $T \rightarrow 0$, $C_p \rightarrow C_v$, or at absolute zero, $C_p = C_v$

Special case,

For water, at 4°C, density is maximum (or specific volume is minimum), $\left(\frac{\partial V}{\partial T}\right)_p = 0$ and

$$C_p = C_v$$

For an ideal gas, $pV = mRT$

$$V = \frac{mRT}{p}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{mR}{p} = \frac{V}{T}$$

Also,

$$p = \frac{mRT}{V}$$

$$\Rightarrow \left(\frac{\partial p}{\partial V}\right)_T = -\frac{mRT}{V^2}$$

$$\therefore C_p - C_v = -T \left\{ -\frac{mRT}{V^2} \right\} \left\{ \left(\frac{V}{T}\right)^2 \right\}$$

$$\therefore C_p - C_v = mR$$

$$c_p - c_v = R$$

The volume expansivity β is defined as

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

The isothermal compressibility k_T is defined as

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$\therefore C_p - C_v = \frac{TV\beta^2}{k_T}$$

Clausius Clapeyron Equations

During phase transitions like melting, vaporization and sublimation, the temperature and pressure remains constant, while the entropy and the volume change.

For a reversible phase transition, the heat transferred is the latent heat, given by

$$l = dq = Tds = T(s^{(f)} - s^{(i)})$$

Now,

$$s = s(v, T)$$

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

Phase transition is

1. Reversible
2. Isothermal ($dT = 0$)
3. Isobaric

$$\therefore ds = \left(\frac{\partial s}{\partial v} \right)_T dv$$

The third Maxwell's relation gives,

$$\left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial S}{\partial V} \right)_T$$

$$\frac{ds}{dv} = \left(\frac{\partial p}{\partial T} \right)_v$$

$$ds = \left(\frac{\partial p}{\partial T} \right)_v dv$$

Since pressure and temperature are constant, by definition the derivative of pressure with respect to temperature does not change. Therefore, the partial derivative of specific entropy may be changed into a total derivative

$$\Delta s = \frac{dp}{dT} \Delta v$$

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

Where Δs and Δv are respectively the change in specific entropy and specific volume.

$$\frac{dp}{dT} = \frac{T\Delta s}{T\Delta v} = \frac{\Delta q}{T\Delta v} = \frac{l}{T\Delta v}$$

For a phase transition process, the heat absorbed or liberated, ΔQ is the Latent Heat of Phase Transition L

$$\therefore \boxed{\frac{dp}{dT} = \frac{l}{T\Delta v}}$$

This result (also known as the *Clausius-Clapeyron* equation) equates the slope of the tangent to the coexistence curve $\frac{dp}{dT}$, at any given point on the curve, to the function $\frac{l}{T\Delta v}$ of the specific latent heat l , Temperature T , and change in specific volume Δv .

Equation of Internal Energy (Energy Equation)

For a system undergoing an infinitesimal reversible process between two equilibrium states,

$$dQ = dU + pdV = TdS$$

$$dU = TdS - pdV$$

The first TdS equation gives,

$$TdS = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dV$$

$$\therefore dU = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dV - pdV = C_v dT + [T \left(\frac{\partial p}{\partial T} \right)_v - p] dV$$

If

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Comparing the coefficients of dV in the preceding two equations, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

This is known as the *energy equation*.

Applications of Energy Equation

For an ideal gas,

$$\begin{aligned} pV &= n\bar{R}T \\ p &= \frac{n\bar{R}T}{V} \\ \therefore \left(\frac{\partial p}{\partial T}\right)_V &= \frac{n\bar{R}}{V} = \frac{p}{T} \\ \left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial p}{\partial T}\right)_V - p = T \left(\frac{p}{T}\right) - p = 0 \\ \therefore \left(\frac{\partial U}{\partial V}\right)_T &= 0 \end{aligned}$$

i.e. U , Internal Energy, does not change when Volume, V , changes at constant temperature.

Again, if Temperature, T is dependent on internal energy, U , pressure p and volume V

$$\begin{aligned} T &\text{ a } U, p, V \\ \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial U}\right)_T &= 1 \\ \therefore \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T &= \left(\frac{\partial U}{\partial V}\right)_T \end{aligned}$$

And

$$\begin{aligned} \boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0} \\ \therefore \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = 0 \end{aligned}$$

Now, $\left(\frac{\partial p}{\partial V}\right)_T \neq 0$, for an isothermal process, the pressure changes for any change in volume and vice versa. Hence,

$$\boxed{\left(\frac{\partial U}{\partial p}\right)_T = 0}$$

i.e. U , Internal Energy, does not change when pressure, p , changes at constant temperature.

Therefore, internal energy is a function of temperature only.

For an ideal gas,

$$dU = C_v dT + [T \left(\frac{\partial p}{\partial T} \right)_V - p] dV$$

And,

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

Therefore, the equation,

$$dU = C_v dT + [T \left(\frac{\partial p}{\partial T} \right)_V - p] dV$$

Becomes,

$$dU = C_v dT$$

This equation holds good for an ideal gas in any process (even if the volume is changing), but for any other substance the equation is true only when the volume is constant, i.e. $dV = 0$.

Similarly,

$$H = U + pV$$

$$dH = dU + pdV + Vdp = dQ + Vdp = TdS + Vdp$$

The second TdS equation gives,

$$\begin{aligned} TdS &= C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \\ \therefore dH &= C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp + Vdp \\ dH &= C_p dT + [V - T \left(\frac{\partial V}{\partial T} \right)_p] dp \end{aligned}$$

Imagine,

$$\begin{aligned} H &= H(T, p) \\ dH &= \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp \end{aligned}$$

Comparing the two equations for dH and equating the terms of dp , we get

$$\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p$$

For an ideal gas,

$$pV = n\bar{R}T$$

$$V = \frac{n\bar{R}T}{p}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{n\bar{R}}{p} = \frac{V}{T}$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = V - T \frac{V}{T} = 0$$

i.e. *Enthalpy* does not change with a change in *pressure* when the *temperature* is constant.

Again, if Temperature, T is dependent on Enthalpy, H , pressure p and volume V

$$T \text{ a } H, p, V$$

$$\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial H}\right)_T = 1$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial H}{\partial V}\right)_T$$

And

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = 0}$$

$$\therefore \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T = 0$$

$$\left(\frac{\partial V}{\partial p}\right)_T \neq 0,$$

$$\therefore \boxed{\left(\frac{\partial H}{\partial V}\right)_T = 0}$$

i.e. *Enthalpy* does not change with a change in *volume* when the *temperature* is constant.

That is enthalpy of an ideal gas is not a function of either volume or pressure, but a function of temperature alone.

Another important point.

$$pV = n\bar{R}T$$

And,

$$V - T \left(\frac{\partial V}{\partial T}\right)_p = 0$$

Therefore, the equation,

$$dH = C_p dT + [V - T \left(\frac{\partial V}{\partial T} \right)_p] dp$$

Becomes,

$$dH = C_p dT$$

This equation holds good for an ideal gas in any process (even if the pressure is changing), but for any other substance the equation is true only when the pressure is constant, i.e. $dp = 0$.

Equation of entropy

$$T ds = du + pdv = du + pdv + vdp - vdp$$

$$T ds = dh - vdp$$

For an ideal gas, $du = c_v dT$, $dh = c_p dT$, and $pv = RT$

$$\therefore ds = \frac{du}{T} + \frac{p}{T} dv = c_v \frac{dT}{T} + R \frac{dv}{v},$$

$$\boxed{\therefore s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}}$$

$$\therefore ds = \frac{dh}{T} - \frac{v}{T} dp = c_p \frac{dT}{T} - R \frac{dp}{p},$$

$$\boxed{\therefore s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}}$$

Since $R = c_p - c_v$

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + (c_p - c_v) \ln \frac{v_2}{v_1} = c_v \left(\ln \frac{T_2}{T_1} - \ln \frac{v_2}{v_1} \right) + c_p \ln \frac{v_2}{v_1}$$

$$\therefore \frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}, \frac{p_2}{p_1} = \frac{T_2 / T_1}{v_2 / v_1}$$

$$\therefore \ln \left(\frac{p_2}{p_1} \right) = \ln \left(\frac{T_2}{T_1} \right) - \ln \left(\frac{v_2}{v_1} \right)$$

$$\boxed{\therefore s_2 - s_1 = c_v \ln \frac{p_2}{p_1} + c_p \ln \frac{v_2}{v_1}}$$

Any one of these equations may be used for computing of entropy between two states of an ideal gas.

$$\frac{\text{Actual Heat Released}}{\text{Theoretical Heating Value}}$$

