THERMODYNAMICS

(For B.E./B.Tech Engineering Students)

As per New Revised Syllabus of
JNTU - Hydrabad, Kakinada & Anantapur

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SYLLABUS
II Year - I Semester- JNTU - KAKINADA
THERMODYNAMICS


UNIT – I

Introduction: Basic Concepts: System, Control Volume, Surrounding, Boundaries, Universe,
Types of Systems, Macroscopic and Microscopic viewpoints, Concept of Continuum, Thermodynamic
Equilibrium, State, Property, Process, Exact & Inexact Differentials, Cycle – Reversibility – Quasi –
static Process, Irreversible Process, Causes of Irreversibility – Energy in State and in Transition,
Types, Displacement& Other forms of Work, Heat, Point and Path functions, Zeroth Law of
Thermodynamics – Concept of Temperature – Principles of Thermometry – Reference Points – Const.
Volume gas Thermometer – Scales of Temperature, Ideal Gas Scale

UNIT - II

PMM I - Joule's Experiments – First law of Thermodynamics – Corollaries – First law applied
to a Process – applied to a flow system – Steady Flow Energy Equation. Limitations of the First
Law – Thermal Reservoir, Heat Engine, Heat pump , Parameters of performance, Second Law of
Thermodynamics, Kelvin-Planck and Clausius Statements and their Equivalence / Corollaries, PMM
of Second kind, Carnot's principle, Carnot cycle and its specialties, Thermodynamic scale of
Temperature, Clausius Inequality, Entropy, Principle of Entropy Increase – Energy Equation,
Availability and Irreversibility – Thermodynamic Potentials, Gibbs and Helmholtz Functions, Maxwell
Relations – Elementary Treatment of the Third Law of Thermodynamics

UNIT – III

Pure Substances, p-V-T- surfaces, T-S and h-s diagrams, Mollier Charts, Phase
Transformations – Triple point at critical state properties during change of phase, Dryness Fraction
– Clausius – Clapeyron Equation Property tables. Mollier charts – Various Thermodynamic processes
and energy Transfer – Steam Calorimetry. Perfect Gas Laws – Equation of State, specific and
Universal Gas constants – various Nonflow processes, properties, end states, Heat and Work
Transfer, changes in Internal Energy –Throttling and Free Expansion Processes – Flow processes

UNIT - IV

Deviations from perfect Gas Model – Vader Waals Equation of State – Compressibility charts
– variable specific Heats – Gas Tables Mixtures of perfect Gases – Mole Fraction, Mass friction
Gravimetric and volumetric Analysis – Dalton’s Law of partial pressure, Avogadro’s Laws of additive
volumes – Mole fraction , Volume fraction and partial pressure, Equivalent Gas const. And Molecular
Internal Energy, Enthalpy, sp. Heats and Entropy of Mixture of perfect Gases and Vapour,
Atmospheric air - Psychrometric Properties – Dry bulb Temperature, Wet Bulb Temperature, Dew
point Temperature, Thermodynamic Wet Bulb Temperature, Specific Humidity, Relative Humidity,
saturated Air, Vapour pressure, Degree of saturation – Adiabatic Saturation , Carrier’s Equation –
Psychrometric chart.

UNIT - V

Power Cycles: Otto, Diesel, Dual Combustion cycles, Sterling Cycle, Atkinson Cycle,
Ericsson Cycle, Lenoir Cycle – Description and representation on P-V and T-S diagram, Thermal
Efficiency, Mean Effective Pressures on Air standard basis – comparison of Cycles.

Refrigeration Cycles: Brayton and Rankine cycles – Performance Evaluation – combined
cycles, Bell-Coleman cycle, Vapour compression cycle-performance Evaluation.
JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY
ANANTAPUR
B.Tech. II - I Sem. (13A03302) THERMODYNAMICS

UNIT I

WORK & HEAT TRANSFER: Work transfer, types of work transfers, Point and Path Functions, Heat transfer, Comparison of Work and Heat transfers.

UNIT II
FIRST LAW OF THERMODYNAMICS: First Law applied to a process and a cycle, Energy - a property, Forms and transformation of Energy, Internal Energy and Enthalpy, PMM I.


UNIT III

Entropy: Clausius' Theorem, Entropy as a property, T-s Plot, Clausius Inequality, Principle of Entropy Increase and its applications. Available Energy, Quality of Energy, definitions of Dead state, Availability.

UNIT IV
Pure Substances: P-v, P-T, T-s diagrams of Pure Substances, Mollier Diagram, Dryness Fraction, Use of Steam Tables for Thermodynamic Properties Thermodynamic Relations: Maxwell's equations, TDS equations, Joule-Kelvin Effect, Clausius-clapeyron equation.

UNIT V
## 1. Basic Concepts and Zeroth Law of Thermodynamics

1.1 Introduction ................................................................. 1.1
1.2 Role of Thermodynamics in Engineering and Science .... 1.2
1.3 Applications of Thermodynamics................................. 1.2
1.4 Founders of Thermodynamics........................................ 1.3
1.5 Basic Concepts............................................................. 1.4
  1.5.1 Units and Dimensions.............................................. 1.4
  1.5.2 Mass....................................................................... 1.4
  1.5.3 Force ...................................................................... 1.4
  1.5.4 Pressure ................................................................. 1.5
  1.5.5 Temperature ............................................................ 1.6
  1.5.6 Specific Volume and Density................................. 1.6
  1.5.7 Energy...................................................................... 1.7
  1.5.8 Power ................................................................... 1.7
  1.5.9 Dimensional Homogeneity .................................... 1.7
1.6 Macroscopic And Microscopic Viewpoints ................. 1.8
  1.6.1 Macroscopic viewpoint ............................................ 1.8
  1.6.2 Microscopic viewpoint ........................................... 1.8
1.7 Concept of Continuum.................................................. 1.9
1.8 Thermodynamic Systems............................................ 1.10
  1.8.1 Types of system..................................................... 1.10
1.9 Closed System............................................................ 1.10
1.10 Open System............................................................. 1.11
1.11 Isolated System.......................................................... 1.11
1.12 Homogeneous and Heterogeneous Systems................. 1.11
  1.12.1 Pure substance..................................................... 1.12
  1.12.2 State postulate...................................................... 1.12
1.13 Property .................................................................... 1.12
1.33.7 Work Associated with the stretching of a
Liquid Film.............................................................. 1.39

1.33.8 Work done per unit volume on a magnetic
material...................................................................... 1.40

1.34 Free Expansion Work................................................. 1.41

1.35 Heat............................................................................. 1.42

  1.35.1 Heat Transfer – A Path Function...................... 1.44

1.36 Heat Capacity............................................................... 1.45

1.37 Reversible and Irreversible Process.............................. 1.45

---

2. First Law of Thermodynamics

2.1 First Law of Thermodynamics.................................... 2.1

2.2 Joules Experiment....................................................... 2.2

2.3 Perpetual Motion of Machine of First Kind................. 2.3

2.4 First Law for a Closed System Undergoing Change
of State................................................................. 2.3

  2.4.1 Internal Energy.................................................. 2.3

  2.4.2 Energy - A property of the system...................... 2.4

2.5 Specific Heat Capacities.............................................. 2.8

  2.5.1 Specific heat...................................................... 2.8

  2.5.2 Latent heat......................................................... 2.9

  2.5.3 Specific heat at constant volume......................... 2.9

  2.5.4 Enthalpy............................................................ 2.10

  2.5.5 Specific heat at constant pressure....................... 2.10

2.6 Thermodynamic Processes.......................................... 2.11

2.7 Application of First Law to Non-flow Process (or)
Closed System......................................................... 2.11

  2.7.1 Constant Volume Process (or) isochoric Process.... 2.12

  2.7.2 Constant Pressure Process (or) isobaric Process.... 2.15
2.7.3 Constant Temperature Process (or) isothermal Process .............................................. 2.18
2.7.4 Reversible Adiabatic Process (or) isentropic Process .................................................... 2.22
2.7.5 Polytropic process ............................................................................................................ 2.26

2.8 Application of First Law to Steady Flow Process
(Open System) ....................................................................................................................... 2.66
2.8.1 Nozzle ............................................................................................................................ 2.69
2.8.2 Diffusor .......................................................................................................................... 2.69
2.8.3 Throttling Device .......................................................................................................... 2.71
2.8.4 Turbine .......................................................................................................................... 2.71
2.8.5 Compressor .................................................................................................................... 2.74
2.8.6 Heat Exchanger .............................................................................................................. 2.75

2.9 Application of First Law to the Transient Flow (or) Unsteady Flow Processes .............................. 2.88
2.9.1 Energy analysis of variable flow processes ..................................................................... 2.89
2.9.2 The filling process ......................................................................................................... 2.90
2.9.3 The emptying process .................................................................................................... 2.91

2.10 Limitations of First Law of Thermodynamics ....................................................................... 2.98

3. Second Law of Thermodynamics

3.1 Introduction to the Second Law of Thermodynamics ............................................................. 3.1
3.2 Thermal Energy Reservoirs .................................................................................................. 3.2
3.3 Heat Engines ........................................................................................................................ 3.2
3.3.1 Thermal efficiency ......................................................................................................... 3.3
3.4 The Second Law of Thermodynamics: Kelvin-Planck Statement ................................................. 3.5
3.5 The Second Law of Thermodynamics: Clausius Statement ....................................................... 3.6
3.6 Refrigerators and Heat Pumps .............................................................................................. 3.7
3.6.1 Refrigerator .................................................................................................................... 3.7
3.6.2 Heat Pump ................................................................. 3.8
3.7 Coefficient of Performance - Cop .................................. 3.9
3.8 Equivalence of The Two Statements .............................. 3.10
3.9 Perpetual-motion Machines ......................................... 3.11
3.10 Reversibility and Irreversibility ................................. 3.11
  3.10.1 Reversibilities ....................................................... 3.12
  3.10.2 Irreversibilities ....................................................... 3.12
    3.10.2.1 Types of Irreversibility ............................... 3.14
3.11 Carnot Cycle ............................................................ 3.14
3.12 Reversed Carnot Cycle .............................................. 3.21
3.13 The Carnot Principles (or) Carnot Theorem .................. 3.21
3.14 Absolute Thermodynamic Temperature Scale ............... 3.24
3.15 Efficiency of The Carnot Heat Engine ......................... 3.27
3.16 The Cop of The Carnot Refrigerator and Heat Pump ....... 3.28
  3.16.1 Reversed Heat engines .......................................... 3.30
3.17 Corollaries of Carnot’s Theorem ................................. 3.33
3.18 Equality of Thermodynamic Temperature Scale With Perfect Gas Scale ........................................... 3.34
  3.18.1 Absolute zero ...................................................... 3.35
3.19 Clausius Inequality .................................................... 3.36
3.20 Concept of Entropy .................................................... 3.42
  3.20.1 Characteristics of entropy .................................... 3.44
  3.20.2 Entropy Transfer with Heat Flow ............................ 3.46
3.21 Principle of Increase of Entropy ................................. 3.47
3.22 Property Diagrams Involving Entropy ......................... 3.49
3.23 What Is Entropy? ...................................................... 3.50
3.24 Entropy Change of Ideal Gas ..................................... 3.52
3.25 Entropy Balance ....................................................... 3.68
3.26 Entropy Generation ................................................... 3.70
3.27 Third Law of Thermodynamics ................................... 3.100
### 3.27.1 Fowler–Guggenheim statement of the third law

3.100

### 3.27.2 Nernst-Simon statement of the third law

3.101

#### 4. Exergy

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>4.1</td>
</tr>
<tr>
<td>4.1.1 High grade energy</td>
<td>4.1</td>
</tr>
<tr>
<td>4.1.2 Low grade energy</td>
<td>4.1</td>
</tr>
<tr>
<td>4.1.3 Available energy</td>
<td>4.1</td>
</tr>
<tr>
<td>4.1.4 Unavailable energy</td>
<td>4.2</td>
</tr>
<tr>
<td>4.2 Law of Degradation of Energy</td>
<td>4.2</td>
</tr>
<tr>
<td>4.3 Availability - Exergy - Work Potential of Energy</td>
<td>4.2</td>
</tr>
<tr>
<td>4.4 Useful Work</td>
<td>4.3</td>
</tr>
<tr>
<td>4.4.1 Actual work</td>
<td>4.3</td>
</tr>
<tr>
<td>4.4.2 Surrounding work</td>
<td>4.3</td>
</tr>
<tr>
<td>4.4.3 Reversible work</td>
<td>4.4</td>
</tr>
<tr>
<td>4.4.4 The Rate of Irreversibility of a Heat Engine</td>
<td>4.4</td>
</tr>
<tr>
<td>4.5 Dead State</td>
<td>4.5</td>
</tr>
<tr>
<td>4.6 Exergy Analysis</td>
<td>4.6</td>
</tr>
<tr>
<td>4.7 Available Energy Referred to a Cycle</td>
<td>4.6</td>
</tr>
<tr>
<td>4.8 Availability of a Closed System</td>
<td>4.8</td>
</tr>
<tr>
<td>4.8.1 Availability function of a closed system with reference to dead state</td>
<td>4.10</td>
</tr>
<tr>
<td>4.8.2 Maximum useful work</td>
<td>4.11</td>
</tr>
<tr>
<td>4.9 Maximum Work in a Reversible Process</td>
<td>4.11</td>
</tr>
<tr>
<td>4.10 Availability of An Open System (Steady Flow Process)</td>
<td>4.12</td>
</tr>
<tr>
<td>4.10.1 Availability function of a open system with reference to dead state</td>
<td>4.13</td>
</tr>
<tr>
<td>4.11 Irreversibility</td>
<td>4.14</td>
</tr>
<tr>
<td>4.11.1 Gouy-Stodola theorem</td>
<td>4.15</td>
</tr>
</tbody>
</table>
4.12 Effectiveness ................................................................. 4.15
4.13 Exergy Destruction .......................................................... 4.16
\hspace{1cm} 4.13.1 Important Hints about Availability ................. 4.16

5. Properties of Pure Substance

5.1 Properties of Pure Substances ........................................... 5.1
5.2 Thermodynamic Properties of Pure Substances in
\hspace{1cm} Solid, Liquid and Vapour Phases ................................. 5.1
5.3 Saturated Vapour and Superheated Vapour ....................... 5.2
5.4 Saturation Temperature and Saturation Pressure ............... 5.4
5.5 Property Diagrams For Phase-change Processes ............... 5.4
\hspace{1cm} 5.5.1 T-v Diagram ...................................................... 5.4
\hspace{1cm} 5.5.2 P-v Diagram ...................................................... 5.7
\hspace{1cm} 5.5.3 P-T Diagram ...................................................... 5.9
\hspace{1cm} 5.5.4 T-s Diagram ...................................................... 5.10
\hspace{1cm} 5.5.5 h-s Diagram or Mollier Diagram ....................... 5.12
\hspace{1cm} 5.5.6 T-h diagram ...................................................... 5.14
5.6 P-v-T Surfaces .................................................................. 5.15
5.7 Thermodynamic Properties of Steam ............................... 5.17
\hspace{1cm} 5.7.1 Property Tables ................................................... 5.17
\hspace{1cm} 5.7.2 Saturated Liquid and Saturated Vapour States ...... 5.17
\hspace{1cm} 5.7.3 Saturated Liquid-Vapour Mixture ....................... 5.18
\hspace{1cm} 5.7.4 Superheated Vapour ............................................. 5.18
\hspace{1cm} 5.7.5 Thermodynamic properties of steam ................... 5.19
5.8 Calculation of Workdone and Heat Transfer in Non-flow
\hspace{1cm} and Flow Processes ..................................................... 5.37
\hspace{1cm} 5.8.1 Constant volume process ..................................... 5.37
\hspace{1cm} 5.8.2 Constant pressure process .................................... 5.42
\hspace{1cm} 5.8.3 Isothermal process and hyperbolic process ............ 5.44
\hspace{1cm} 5.8.4 Isentropic process ............................................... 5.46
### 5.8.5 Throttling process

- **5.8.5.1 Throttling Calorimeter**
- **5.8.5.2 Separating and Throttling Calorimeter**

### 5.9 Standard Rankine Cycle

- **5.9.1 The Ideal Cycle for Vapour Power Cycles**
- **5.9.2 Efficiency of Standard Rankine Cycle**

### 5.10 Rankine Cycle - Reheating Cycle

- **5.10.1 Advantages (or) Effects of Re-heating**

### 5.11 Re-generation: Regenerative Cycle (Bleeding Cycle)

- **5.11.1 Advantages of Regenerative cycle**

### 5.12 Binary Vapour Cycle and Combined Cycle

### 6. Behaviour of Ideal and Real Gases

- **6.1 Gas Mixtures**
- **6.2 Composition of a Gas Mixtures**
- **6.3 Relationship Among Properties**
- **6.4 Mole Fraction**
- **6.5 Mass Fraction**
- **6.6 Relationship Between Mass and Mole Fractions**
- **6.7 Properties of Ideal Gas**
  - **6.7.1 Equation of state**
- **6.8 Avogadro’s Law**
- **6.9 Universal Gas Constant and Characteristic Gas Constant**
- **6.10 Partial Pressure**
- **6.11 Partial Volume**
- **6.12 Dalton’s Law of Partial Pressure**
- **6.13 Amagat’s Law of Partial Volume**
- **6.14 Properties of Gas Mixtures**
- **6.15 Molar Mass of a Gas Mixture**
- **6.16 Gas Mixture Constants**
- **6.17 Gibbs–Dalton’s Law**
- **6.18 Properties of Real Gas**
- **6.19 Vander Waal's Equation of State**
  - **6.19.1 Berthelot equation of state**
6.19.2 Dieteric equation of state ........................................ 6.40
6.19.3 Redlich-Kwong equation of state ............................. 6.41
6.20 Compressibility Factor .................................................. 6.41
6.20.1 Virial expansions...................................................... 6.42
6.20.2 Compressibility Chart .............................................. 6.43
6.21 Phase Change Process .................................................. 6.46
6.22 Kay’s Rule ...................................................................... 6.46
6.23 Comparison Between Ideal and Real Gases ................. 6.49

7. Thermodynamic Relations

7.1 Introduction ................................................................. 7.1
7.2 Fundamental Mathematical Theorems ......................... 7.1
7.3 Maxwell's Equations..................................................... 7.3
7.4 Tds Relations ............................................................... 7.5

7.4.1 Entropy Equations ..................................................... 7.5

7.4.1.1 First Tds equation .............................................. 7.5
7.4.1.2 Second Tds equations ........................................ 7.6
7.5 Equations For Internal Energy, Enthalpy and Entropy .... 7.7

7.5.1 Internal energy equation ......................................... 7.7
7.5.2 Enthalpy equation .................................................... 7.7
7.5.3 Entropy equations ................................................... 7.8

7.6 Specific Heat Relations................................................ 7.8

7.6.1 Specific heat at constant volume ............................... 7.8
7.6.2 Specific heat at constant pressure ............................. 7.8
7.6.3 Specific heats difference .......................................... 7.8
7.6.4 Ratio of specific heats ............................................ 7.11

7.7 The Clapeyron Equation (Clausius Clapeyron Equation) 7.12
7.8 Throttling Process ........................................................ 7.14
7.9 Joule Kelvin Effect and Inversion Curves ..................... 7.14
7.10 Co-efficient of Volume Expansion .............................. 7.18
7.11 Isothermal Compressibility ....................................... 7.18
8. Psychrometry

8.1 Psychrometry

8.1.1 Uses of Psychrometry

8.2 Psychrometric Parameters

8.2.1 Measurement of Parameters

8.3 Psychrometric Properties

8.3.1 Dalton’s Law

8.3.2 Partial Pressure

8.3.3 Specific humidity (or) Humidity ratio (or) Moisture content: (ω)

8.3.4 Degree of saturation (or) Percentage humidity (μ)

8.3.5 Relative humidity (RH), φ

8.4 Property Calculations of Air Vapour Mixtures (Using Formula)

8.5 Psychrometric Charts

8.6 Calculation of Parameters Using Psychrometric Charts

8.6.1 To Read Wet Bulb temperature

8.6.2 To Read Dew Point Temperature

8.6.3 To Read Specific Humidity

8.6.4 To Read Enthalpy

8.7 Psychrometric Process

8.7.1 Sensible Heating Process

8.7.2 Sensible Cooling Process

8.7.3 Cooling and Dehumidification (‘t’ decreases and ‘ω’ decreases)

8.7.4 Cooling and Humidification: (‘t’ decreases and ‘ω’ increases)

8.7.5 Heating and Dehumidification

8.7.6 Heating and Humidification

8.7.7 Adiabatic [No heat transfer] Saturation Process

8.7.8 Adiabatic Mixing of Two Air Streams
9. Gas Power Cycles

9.1 Gas Power Cycles

9.2 Different Types of Air Standard Cycles
   9.2.1 Air Standard Efficiency

9.3 Carnot Cycle

9.4 Stirling Cycle

9.5 Ericsson Cycle

9.6 Otto Cycle (or) Constant Volume Cycle

9.7 Diesel Cycle or Constant Pressure Cycle

9.8 Dual Combustion Cycle

9.9 Comparison of Otto, Diesel And Dual Combustion Cycles

9.10 Atkinson Cycle

9.11 Lenoir Cycle

10. Brayton Cycles and Refrigeration Cycles

10.1 Brayton Cycle - Ideal Gas Turbine Cycle
   10.1.1 Gas turbine Open cycle
   10.1.2 Gas turbine Closed cycle

10.2 Optimum Pressure Ratio for Maximum Specific Work Output

10.3 Bell-coleman Cycle

10.4 Vapour Compression Refrigeration
   10.4.1 Different Conditions of the Vapour

10.5 Performance Evaluation - Factors Affecting
   Performance Of A Vapour Compression System
   10.5.1 Calculations in a vapour compression refrigeration system
Chapter 1
Basic Concepts and Zeroth Law of Thermodynamics

1.1 INTRODUCTION

Thermodynamics can be defined as the science which deals with the transformation of energy and its effects on the properties of the substance. The word ‘Thermodynamics’ originates from two Greek words, ‘therme’ (heat) and ‘dynamis’ (motion or power). Thermodynamics can also be called as the science of 3E’s i.e., Equilibrium, Energy and Entropy.

Thermodynamics is a branch of Science that deals with the relationship among heat, work and properties of system which are in equilibrium with one another.

One of the most fundamental laws of nature is the conservation of energy principle. It states that during an interaction, energy can change from one form to another but the total amount of energy remains constant. i.e., Energy can neither be created nor be destroyed, but it can be transformed from one form to another. For example,

1. A ball falling from a tower picks speed as a result of its potential energy being converted to kinetic energy.

2. A person eating more and working less i.e., a person who has a greater energy input (food) than energy output (exercise) will gain weight (store energy in the form of fat)

The first law of thermodynamics is based on the conservation of energy principle. The second law of thermodynamics reveals that energy has quality as well as quantity and actual processes occur in the direction of decreasing quality of energy. For example, a cup of hot coffee in a room eventually cools, but a cup of cool coffee never gets hot by itself.

The first and second laws of thermodynamics emerged simultaneously in the 1850s, by the works of James Prescott Joule, William Rankine, Rudolph Clausius and Lord Kelvin.
1.2 ROLE OF THERMODYNAMICS IN ENGINEERING AND SCIENCE

Thermodynamics plays a vital role in the field of Engineering and Science. They are explained as follows.

Thermodynamics is very important in the design, analysis and development of Engineering systems such as the power-producing systems like engines, turbines etc. and the power-consuming systems like compressor, pumps, etc.

The working principle of many scientific devices like thermometer, thermistor, thermostat etc... involves thermodynamics.

Good understanding and careful applications of the fundamentals of thermodynamics leads to improved design, increased efficiency, optimum operating conditions and decreased levels of environmental pollution etc.

1.3 APPLICATIONS OF THERMODYNAMICS

Thermodynamic principles are applied in various fields of Engineering and Technology. Some of the fields are

(i) Internal combustion engine (ii) Gas turbines
(iii) Air conditioner & Refrigerator (iv) Compressor
(v) Steam and Nuclear power plants (vi) Rockets
(vii) Jet engines etc.

Applications of thermodynamics are found in various aspects of life eg: A commonly encountered thermodynamics application is, ‘the human heart, which is constantly pumping blood to all parts of the body. The movement of blood and various energy conversions generates heat, within the body. (normally called as body heat). The generated heat is constantly rejected to the environment and the process is called as metabolic heat rejection. However, this heat rejection can be controlled by adjusting our clothing to the environment conditions.

Other application of thermodynamics involves increasing the heat transfer rate like exhaust fan in a house, cooling fans in the computer CPU and fins provided on the engine cylinders etc.
### 1.4 FOUNDERS OF THERMODYNAMICS

<table>
<thead>
<tr>
<th>Founders</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Antoine Laurent Lavoisier</td>
<td>- Father of Modern Chemistry</td>
</tr>
<tr>
<td>(1743 - 1794)</td>
<td>- Developed combustion process</td>
</tr>
<tr>
<td></td>
<td>- Also, proposed the name for ‘oxygen’ (which was discovered by Joseph</td>
</tr>
<tr>
<td></td>
<td>priestely) and mentioned its importance in the combustion process.</td>
</tr>
<tr>
<td>2. Nicolas Leonard Sadi Carnot</td>
<td>- Father of Thermodynamics</td>
</tr>
<tr>
<td>(1796 - 1832)</td>
<td>- Developed carnot cycle</td>
</tr>
<tr>
<td></td>
<td>- Established the basic principles governing the conversion of heat to work,</td>
</tr>
<tr>
<td></td>
<td>that led to the fundamental laws of thermodynamics.</td>
</tr>
<tr>
<td>3. James Prescott Joule</td>
<td>- Established ‘heat’ as a form of energy which led to the dismissal of ‘calorific</td>
</tr>
<tr>
<td>(1818 - 1889)</td>
<td>theory of heat’.</td>
</tr>
<tr>
<td></td>
<td>- Developed ‘First law of Thermodynamics’ with experimental proof that</td>
</tr>
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<td></td>
<td>supports the heat, is also an energy.</td>
</tr>
<tr>
<td>4. William Thompson (also called</td>
<td>- Absolute temperature scale is named after him.</td>
</tr>
<tr>
<td>as Lord Kelvin ) (1829 - 1907)</td>
<td>- Developed Thermodynamic temperature scale.</td>
</tr>
<tr>
<td></td>
<td>- Along with joule, he expounded Joule-Kelvin effect.</td>
</tr>
<tr>
<td>5. Rudolph J. Clausius</td>
<td>- Developed ‘Second Law of Thermodynamics’</td>
</tr>
<tr>
<td>(1822 - 1888)</td>
<td>- Also, led to the founding of the Thermodynamic property called ‘entropy’.</td>
</tr>
</tbody>
</table>
1.5 BASIC CONCEPTS
Some important basic concepts of thermodynamics are discussed in this Chapter.

1.5.1 Units and Dimensions
Nowadays, the SI (System International) system of units has been used. Any physical quantity can be characterised by dimensions. The arbitrary magnitudes assigned to the dimensions are called Units. Some basic dimensions such as mass \( m \), length \( L \), time \( t \) and temperature \( T \) are selected as \textbf{primary (or) fundamental dimensions}, while others such as velocity \( V \), energy \( E \), and volume \( V \) are expressed in terms of primary dimensions and are called \textbf{secondary dimensions} (or) \textbf{derived dimensions}.

A number of unit systems have been developed over the years. But nowadays, the SI (System International) system of units are widely used. The SI is simple and logical system. Some fundamental dimensions and their units in SI are given in the following table.

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Unit</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>metre</td>
<td>m</td>
</tr>
<tr>
<td>Mass</td>
<td>kilogram</td>
<td>kg</td>
</tr>
<tr>
<td>Time</td>
<td>second</td>
<td>s</td>
</tr>
<tr>
<td>Temperature</td>
<td>Kelvin</td>
<td>K</td>
</tr>
<tr>
<td>Electric current</td>
<td>Ampere</td>
<td>A</td>
</tr>
<tr>
<td>Amount of light</td>
<td>Candela</td>
<td>cd</td>
</tr>
<tr>
<td>Amount of matter</td>
<td>mole</td>
<td>mol</td>
</tr>
</tbody>
</table>

1.5.2 Mass \( (m) \)
It is quantity of matter. Its unit is ‘kg’.

1.5.3 Force
In SI, the unit for force is derived from Newton’s second law. i.e., Force = (Mass) \( \times \) (Acceleration)

\[
F = ma
\]

In SI, the force unit is the Newton \( (N) \) and it is defined as the force required to accelerate a mass of 1 kg at a rate of 1 m/s\(^2\). i.e., 1 N = 1 kg \cdot m/s\(^2\)
The weight of a body \((W)\) is the force with which the body is attracted to the centre of the earth. It is the product of its mass \((m)\) and the local gravitational acceleration \((g)\), i.e., \(W = mg\)

where \(g = 9.80665\) (9.81) m/s\(^2\) at sea level. The mass \((m)\) of a body will remain same regardless of its location in the universe. Its weight, however, will change with a change in gravitational acceleration. A body will weigh less on top of a mountain since \(g\) decreases with altitude. At sea level, a mass of 1 kg will weigh 9.807 N.

1.5.4 Pressure

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

If \(\delta A\) is a small area and \(\delta A'\) is the smallest area from the concept of continuum, and \(\delta F_n\) is the component of force normal to \(\delta A\), the pressure \(P\) at a point on the wall is defined as

\[
P = \lim_{\delta A \to \delta A'} \frac{\delta F_n}{\delta A}
\]

The pressure \(P\) at a point in a fluid in equilibrium is the same in all directions.

The unit for pressure in the SI system is the Pascal \((Pa)\), which is the force of 1 N acting on an area of 1 m\(^2\).

\[
1 \text{ Pascal} = 1 \text{ Pa} = 1 \text{ N/m}^2
\]

The unit of pascal is very small. Hence, very often, kilo-pascal (kPa) (or) mega-pascal (MPa) is used. Sometime bar and standard atmosphere are used which are not within the SI system of units.

\[
1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa} = 0.1 \text{ M Pa}
\]

\[
\text{Standard atmosphere} = 1 \text{ atm} = 101.325 \text{ kPa} = 1.01325 \text{ bar}
\]

Most of the instruments indicate pressure relative to the atmospheric pressure where as the pressure of a system is its pressure above zero (or) relative to a perfect vacuum.
The pressure relative to the atmosphere is called gauge pressure.
The pressure relative to a perfect vacuum is called absolute pressure.

\[
\text{Absolute pressure} = \text{Gauge pressure} + \text{Atmospheric pressure}
\]

The SI unit prefixes are used in all branches of engineering. Some standard prefixes in SI units for Mechanical Engineering branch are given in the table.

<table>
<thead>
<tr>
<th>Multiple</th>
<th>Prefix</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{12})</td>
<td>Tera, T</td>
</tr>
<tr>
<td>(10^9)</td>
<td>Giga, G</td>
</tr>
<tr>
<td>(10^6)</td>
<td>Mega, M</td>
</tr>
<tr>
<td>(10^3)</td>
<td>Kilo, k</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>milli, m</td>
</tr>
<tr>
<td>(10^{-6})</td>
<td>micro, (\mu)</td>
</tr>
<tr>
<td>(10^{-9})</td>
<td>nano, n</td>
</tr>
<tr>
<td>(10^{-12})</td>
<td>pico, p</td>
</tr>
</tbody>
</table>

1.5.5 Temperature

It is defined as the degree of intensity of heat or measure of hotness or coldness of a body.

Temperature - Intensive property - °C or K (Centigrade or Kelvin).

\[30°C = 30 + 273 = 303 K\]

Normally, \(t\) is for °C and \(T\) is for K.

1.5.6 Specific Volume and Density

Volume \((V)\) is the space occupied by a substance and is measured in m\(^3\). The specific volume \((v)\) of a substance is defined as the volume per unit mass and is measured in m\(^3\)/kg. From the concept of continuum, the specific volume at a point is defined as

\[v = \lim_{\delta V' \to \delta V} \frac{\delta V}{\delta m}\]

where \(\delta V'\) is the smallest volume for which the system can be considered as continuum.
Specific volume: $\nu$

Volume = Total volume = $V$ in m$^3$

Specific volume = $\frac{\text{Volume}}{\text{mass}} = \frac{V}{m} = \nu$

Its unit is m$^3$/kg

Density $\rho$: It is the mass of the substance per unit volume. Its unit is kg/m$^3$.

Density ($\rho$) is the mass per unit volume of a substance and is given in kg/m$^3$. $\rho = \frac{m}{V}$

1.5.7 Energy

Work, which is a form of energy, can simply be defined as force times distance. Therefore, it has the unit “newton-meter (N-m)” which is called a Joule (J). i.e.,

$1 \text{ J} = 1 \text{ N-m}$

A more common unit for energy in SI is the kilojoule (1 kJ = 10$^3$ J). The energy per unit mass is the specific energy and its unit is J/kg.

In the metric system, the amount of energy needed to raise the temperature of 1 kg of water at 15°C by 1°C is defined as 1 kiloCalorie (kCal), and

$1 \text{ kCal} = 4.187 \text{ kJ}$.

1.5.8 Power

The rate of energy transfer (or) storage is called power. The unit of power is Watts (W), kiloWatts (kW) (or) MegaWatts (MW).

$1 \text{ W} = 1 \text{ J/s} = 1 \text{ Nm/s}$; $1 \text{ kW} = 1000 \text{ W}$

1.5.9 Dimensional Homogeneity

In engineering, all equations must be dimensionally homogeneous, i.e., every term in an equation must have the same unit.

Analyse the following equation, $E = 35 \text{ kJ} + 8 \text{ kJ/kg}$

where $E$ is the total energy in kJ. Since the two terms on the right hand side do not have the same units, they cannot be added to obtain the total energy. Multiplying the last term ($8 \text{ kJ/kg} \times m \text{ kg}$) by mass will eliminate the
kilograms in denominator, and the whole equation will become dimensionally homogeneous i.e., every term in the equation will have the same unit.

\[ E = 35 \text{ kJ} + 8 \text{ mkJ} \]

### 1.6 MACROSCOPIC AND MICROSCOPIC VIEWPOINTS

Normally, a substance consists of a large number of particles called molecules and the properties of substance naturally depend on the behaviour of these particles. There are two points of view from which the behaviour of particles can be studied. They are

<table>
<thead>
<tr>
<th>Viewpoints</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscopic Viewpoint</td>
<td>(or) Classical Thermodynamics</td>
</tr>
<tr>
<td>Microscopic Viewpoint</td>
<td>(or) statistical Thermodynamics</td>
</tr>
</tbody>
</table>

#### 1.6.1 Macroscopic viewpoint

In this point of view, a certain amount of matter is considered, neglecting the events occurring at the molecular level. It does not require a knowledge on the behaviour of individual particles. It provides a direct and easy way to the solution of engineering.

In general, macroscopic point of view is just like, “inventing a device or using an instrument, to measure the quantities directly, instead of finding it out through calculation, derivation and formulas”.

eg: ‘Pressure gauge’ is used to measure pressure directly without calculating force on a given unit area.

Likewise, temperature can also be measured using thermometer.

However, macroscopic point of view is limited to those effects that can be perceived by human senses.

#### 1.6.2 Microscopic viewpoint

In this point of view, behaviour of each molecule has to be studied, to find out the behaviour of the entire substance. Each molecule at a given instant has certain position, velocity and energy, for each molecule these changes frequently as a result of collisions. And also, these effects cannot be perceived by human senses.

In general, microscopic point of view requires large number of data and equations to find out the quantities through calculation and derivation.
eg: Impulse, Enthalpy, Entropy, Gibbs function, Helmhotz function etc.

<table>
<thead>
<tr>
<th>Macroscopic viewpoint</th>
<th>Microscopic viewpoint</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. It is also called as classical thermodynamics.</td>
<td>It is also called as statistical thermodynamics.</td>
</tr>
<tr>
<td>2. Behaviour of each molecule need not to be determined.</td>
<td>Behaviour of each molecule need to be determined.</td>
</tr>
<tr>
<td>3. Molecular effects can be perceived by human senses.</td>
<td>Molecular effects cannot be perceived by human senses.</td>
</tr>
<tr>
<td>4. Classical thermodynamics, however can be derived from statistical thermodynamics.</td>
<td>Statistical thermodynamics cannot be determined using classical thermodynamics.</td>
</tr>
<tr>
<td>5. eg: Pressure, Temperature</td>
<td>eg: Enthalpy, Entropy</td>
</tr>
</tbody>
</table>

1.7 CONCEPT OF CONTINUUM

Generally, matter is made up of atoms & these atoms are widely spaced in the gas phase. From the macroscopic viewpoint, behaviour of individual molecules can be disregarded and the matter with widely spaced atoms can be treated as continuous because a large no. of molecules can accommodate even in an extremely small volume of atom. This view of continuous, homogeneous matter with no holes is called as “continuum”.

The continuum idealization allow us to treat properties as a point function and to assume that the properties vary continuously in space with no jump discontinuities.

Concept of continuum can be verified by the dimensionless parameter known as knudsen number ($k_n$).

$$ k_n = \frac{\text{Mean free path of the molecules}}{\text{Characteristic Length of the system}} = \frac{\lambda}{L} $$

If knudsen number, $k_n < 0.01$, then the concept of continuum holds good, i.e., the continuum model can be applicable as long as the characteristic length of the system is much larger than the mean free path of the molecules.

At very high vacuums or high elevations, the mean free path becomes large, for such cases “rarefield gas flow theory” should be used and the impact of individual molecules should be considered.

But in most engineering applications, however the continuum is valid and convenient & goes hand in hand with the macroscopic point of view.
1.8 THERMODYNAMIC SYSTEMS

Thermodynamic system is known as a space or constrained area upon which our attention is concentrated on. It is the region to be studied. The system has boundary (or) boundary line. Anything outside the boundary is called surroundings. In other words, the system and surroundings are separated by boundary. (Boundary may be real or imaginary).

1.8.1 Types of system

The systems are classified into:

1. Closed system, 2. Open system, 3. Isolated system.

System may be considered to be closed (or) open, depending on whether a fixed mass (or) a fixed volume in space is chosen for study.

1.9 CLOSED SYSTEM

A closed system, also known as a control mass, consists of a fixed amount of mass and no mass can cross its boundary.

i.e., no mass can enter (or) leave a closed system as shown in Fig. 1.3 But energy, in the form of heat (or) work, can cross the boundary. And the volume of a closed system does not
have to be fixed.

Energy is transferred from the surroundings into the system and from the system to the surroundings. But there is no mass transfer in closed system.

Eg. Piston and cylinder without valves Fig. 1.4.

1.10 OPEN SYSTEM

An open system is a properly selected region in space. It usually encloses a device that involves mass flow. A large number of engineering problems involve mass flow in and out of a system and, therefore, are modeled as control volumes. In general, any arbitrary region in space can be selected as a control volume. The boundaries of a control volume are called a control surface as shown in Fig. 1.6 and they can be real (or) imaginary.

Both energy and mass are transferred from the system to surroundings and from the surroundings to system.

(e.g) 1. Air compressor (Fig 1.5), 2. I.C. Engines, 3. Turbines, 4. Boilers, 5. Centrifugal pumps, 6. Nozzles.

Most of the engineering devices are open systems.

1.11 ISOLATED SYSTEM

Neither energy nor mass transfer occurs between the system and surroundings (Fig 1.7).

Practically, no system is isolated.

1.12 HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

A system, which contains only a single phase, is called as Homogeneous system.

Eg. Mixture of air and water vapour.

A system, which consists of more than one phase, is called as Heterogeneous system.

Eg. Mixture of water and steam.
1.12 Pure substance
A Substance with homogeneous and invariable chemical composition even though change of phase takes place is called as pure substance.

Eg. Water.

1.12.2 State postulate
The number of independent intensive properties are required to fix the state of the system is given by state postulate.

For a pure substance, this is called as two property rule. i.e., two intensive properties are required to fix the state of the pure substance.

Number of independent intensive properties can be found analytically using Gibb’s rule

\[ P + F = C + 2 \]

\[ P \text{ - No. of phase, } C \text{ - No. of components} \]
\[ F \text{ - No. of independent intensive properties} \]
\[ \text{eg: For single liquid (or) single gas} \]
\[ P = 1, \quad C = 1 \]
\[ \therefore \quad F = C - P + 2 = 1 - 1 + 2 = 2 \]

1.13 PROPERTY
It is a characteristic of the system. The system is identified by some quantities like temperature, pressure, volume etc.

1. Intensive Property: The properties which do not depend on the mass of the system, are called intensive property.

*Intensive property* - Independent of the mass of the system: Example - Temperature, pressure, density, surface tension, specific gravity, etc.

2. Extensive Property: Those properties which depend on the mass of the system are called extensive property. Example: Volume, Force, eg: electric charge, weight, energy (heat and work) magnetization. If mass is more, then volume will be more. (Fig 1.8).
The extensive property divided by mass will become intensive property.

(e.g) Volume \( (\text{m}^3)/\text{mass} = \text{Specific volume} \ \text{m}^3/\text{kg} \)  

(Extensive) \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quan
Any change that a system undergoes from one equilibrium state to another is called a \textbf{process}, and the series of states through which a system passes during a process is called the \textbf{path} of the process. To describe a process completely, one should specify the initial and final states of the process, as well as the path it follows and the interactions with the surroundings.

Refer the Fig. 1.11

The \textbf{state} is a condition of the system at particular time. Each and every condition of the system is called \textbf{state}.

At state (1), the pressure is $P_1$ and the volume is $V_1$. Similarly at state (2), the pressure is $P_2$ the volume is $V_2$. In between 1 and 2, there are so many states $A, B, C, ... , G$.

So every time the system is under the change of states. If all the states are traced, it is the \textbf{path} of the change of states. If the path is completely specified, the change of state is called \textbf{process}. The example given is a compression process.

\section*{1.15 CYCLE}

The series of processes whose end states are identical, then it is called cycle. Refer Fig 1.12.

$1-2 = \text{The process A}$

$2-1 = \text{The process B}$

$1-2-1 = \text{Cycle}$

The process A and the process B form a cycle. Because initial state is 1 and final state is also 1. So it is a cycle (or) thermodynamic cycle.

A system is said to have undergone a \textbf{cycle}, if it returns to its initial state at the end of the process. That is, for a cycle, the initial and final states are identical.
1.16 THERMODYNAMIC EQUILIBRIUM

When mechanical equilibrium, chemical equilibrium and thermal equilibrium are satisfied, then the system is said to be in thermodynamic equilibrium.

When any property remains same with respect to time, it is called as equilibrium or steady state.

Eg. Temperature and pressure at all points of a system are same means that the system exists in thermodynamic equilibrium.

1. Mechanical Equilibrium

If the system's pressure remains same with respect to time, then the system is said to be in mechanical equilibrium.

2. Chemical Equilibrium

If the system's chemical composition remains same with respect to time, then the system is said to be in chemical equilibrium.

3. Thermal Equilibrium

If the system's temperature remains same with respect to time, then the system is said to be in thermal equilibrium.

1.17 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, it is called a quasi-static, (or) quasi-equilibrium process. A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

A quasi-static process is an idealized process and is not a true representation of an actual process. But many actual processes closely approximate it and they can be modeled as quasi-equilibrium with negligible error. Engineers are interested in quasi-equilibrium processes for two reasons as follows.

1. They are easy to analyze.
2. Work-producing devices (like engine) deliver maximum work when they operate on quasi-static processes.

Therefore, quasi-static processes serve as standards to which actual processes can be compared.
Consider a system of gas contained in a cylinder Fig 1.13(a). The system initially is in equilibrium state $P_1, V_1$ and $T_1$. The weight on the piston is balanced by the pressure of the gas. If the weight is removed, there will be an unbalanced force between the system and surroundings, and under the gas pressure, the piston will move up till it hits the stops. The system comes to an equilibrium state - $P_2, V_2$ and $T_2$. But the intermediate states are non-equilibrium states and we cannot define its properties. So these two states (1 and 2) are joined by dotted line.

Now instead of single weight, we can place many number of small weights on the piston Fig 1.13(b). If we remove weights one by one very slowly from the piston, then the piston will move upward very slowly. The change of state of system from equilibrium state is infinitesimally small. So
every state traced by the system is equilibrium state. The process, joined by all the equilibrium states passed by the system is called **quasi-static process**. ['Quasi’ means ‘almost’].

Quasi-static process is a reversible process.

*A process which can be reversed in direction and the system retraces the same equilibrium states is known as reversible process.*

Infinite slowness is the characteristic feature of a quasi-static process.

### 1.18 PATH FUNCTION AND POINT FUNCTION

Refer the [Fig 1.14](#). In this fig, there are many quasi-static paths such as A, B (or) C from state 1 to state 2. Since area under each curve represents the work for each process, the amount of work involved in path A, B and C are not equal. The work is not a function of the end states of the process but it depends on the path the system follows from state 1 to state 2. Hence, work is called a **path function** and \(dW\) is **inexact (or) imperfect differential**.

Thermodynamic properties like pressure, volume and temperature are **point functions**, because, for a given state, there is a definite value for each property. The change of property of a system is independent of the path the system follows during the change of state and it depends only on the initial and final states of the system. Hence \(dV\) (or) \(dP\) is **an exact (or) perfect differentials**.

For example, the integration of property is

\[
\int_{V_1}^{V_2} dV = V_2 - V_1
\]

i.e., Change in volume depends only on the end states of the system irrespective of the path the system follows.

But, workdone in a quasi-static process between two given state depends on the path followed. And the integration of work transfer is
Rather, \[ \int_{1}^{2} dW = W_2 - W_1 \]

### 1.19 ZEROTH LAW OF THERMODYNAMICS

If the systems A and B are in thermal equilibrium separately and A and C are in thermal equilibrium separately, then B and C should be in thermal equilibrium.

This law is the basis for temperature measurement.

#### 1.19.1 Equality of temperature

When two bodies at different temperatures are brought into contact, after some time, they attain a common temperature and are then said to exist in thermal equilibrium.

The zeroth law was first formulated by R.H. Fowler. This law explains the fundamental principles of thermodynamics, but was recognised after the formulation of first and second laws of thermodynamics. So it was named as ‘zeroth law’ since it should have preceded the first and second laws of thermodynamics.

### 1.20 MEASUREMENT OF TEMPERATURE

The temperature of a body can be measured, by using a device known as thermometer. A common thermometer consists of a small amount of mercury in an evacuated glass tube. There are five different kinds of thermometer.

1. Constant volume gas thermometer
2. Constant pressure gas thermometer
3. Electrical resistance thermometer
4. Thermocouple
5. Mercury-in-glass thermometer
1.20.1 Thermometry
Thermometry is the science and practice of temperature measurement. Any measurable change in the thermometric probe (e.g., extension of mercury in the tube of a mercury-in-glass thermometer) can be used to mark temperature levels, that should later be calibrated as an internationally agreed unit (like celsius, Fahrenheit, Kelvin, etc.).

Thermometry is broadly divided into two subfields.
(i) Contact thermometry
(ii) Non-contact thermometry

1.20.2 Applications of thermometry
Temperature is one of the most measured physical parameters in science and technology, but thermometry is not only applied to measuring temperature, but also an indirect measure of many material properties like thermal capacities, relative humidity (by means of wet bulb or dew point temperatures) and enthalpy changes (by thermal analysis).

1.21 THERMOMETRIC PROPERTY
Thermometric property is any physical property that changes measurably with temperature.

eg: Extension of mercury in a mercury-in-glass thermometer

1.21.1 Reference points
A reference point is a ‘basis’ (or) a ‘standard’, for evaluation.

To calibrate the thermometer, first and foremost, we need to define a temperature scale. For defining the temperature scale, we have to choose reference points (reference temperature) also called as the fixed points.

For Example: In the Celsius scale, the fixed points are defined using the properties of pure water.

i.e., the lower fixed point or ice point, is the temperature of pure melting ice at normal atmospheric pressure.

Also, the higher fixed point or steam point, is the temperature of pure boiling water at normal atmospheric pressure.

Fixed point or reference points are classified into two categories.
(i) Two reference points method (or) two fixed points method (method used before 1954)
(ii) One reference point method (or) one fixed points method (method used after 1954)
(i) **Two reference points method**

In this method, two fixed points are used, i.e.,

(a) **Ice point**

Ice point is the temperature at which ice and water are in equilibrium at a pressure of 1 atm pressure.

(b) **Steam point**

Steam point is the temperature at which water vapour condenses at a pressure of 1 atm pressure.

Let $X$ be the thermometric property and $\theta (x)$ be the temperature of the system to be measured, then $\theta (x) = ax$ where $a$ is arbitrary constant.

The thermometer is first placed in contact with system whose temperature $\theta (X)$ to be measured & then in contact with one of the fixed point (steam or ice), whose temperature is $\theta (X_1)$, Thus

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

$$\theta (X_1) \frac{X_1}{X} = \theta (X)$$  \hspace{1cm} (1)

Similarly, the thermometer at the temperature $\theta (s)$ is placed in contact with another fixed point of temperature $\theta (X_2)$. It gives

$$\theta (X_2) \frac{X_2}{X} = \theta (X)$$  \hspace{1cm} (2)

Subtract (2) from (1)

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

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

The temperature interval, $\theta (X_1) - \theta (X_2)$ between these two fixed points was chosen to be 100 degrees. The use of two fixed points was found unsatisfactory and later disregarded.

(ii) **One reference point method**

In this method, only one reference point is used, i.e., the triple point of water.
**Triple point of water:** It is a point at which three phases (solid, liquid and gas) i.e., ice, liquid water and water vapour exist in equilibrium with one another.

The temperature at which, these states exist in equilibrium are 273.16 K or 273.16 degrees Kelvin.

The temperature of triple point of water $\theta_t$ and thermometer properly placed in contact with the body whose temperature $\theta$ to be measured is

$$\theta_t = a X_t \Rightarrow a = \frac{\theta_t}{X_t} = \frac{273.16}{X_t}$$

Therefore, $\theta = a X$

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

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

Therefore, the temperature of the triple point of water is called as the “standard fixed point of thermometry”.

### 1.22 COMPARISON OF THERMOMETER

<table>
<thead>
<tr>
<th>Thermometer</th>
<th>Thermometric property</th>
<th>Temperatures (using one fixed point method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Constant volume gas thermometer</td>
<td>Pressure ($P$)</td>
<td>$Q(P) = 273.16 \frac{P}{P_t}$</td>
</tr>
<tr>
<td>2. Constant pressure gas thermometer</td>
<td>Volume ($V$)</td>
<td>$Q(V) = 273.16 \frac{V}{V_t}$</td>
</tr>
<tr>
<td>3. Electric resistance thermometer</td>
<td>Resistance ($R$)</td>
<td>$Q(R) = 273.16 \frac{R}{R_t}$</td>
</tr>
<tr>
<td>4. Thermocouple</td>
<td>Thermal e.m.f ($E$)</td>
<td>$Q(E) = 273.16 \frac{E}{E_t}$</td>
</tr>
<tr>
<td>5. Liquid-in-glass thermometer</td>
<td>Length ($L$)</td>
<td>$Q(L) = 273.16 \frac{L}{L_t}$</td>
</tr>
</tbody>
</table>
1.23 EQUATION OF STATE

The equation which relates the properties $P$, $v$, and $T$ is known as an Equation of state.

\[ f(P, v, T) = 0 \]

The simplest form of equation of state for the ideal gas is given below.

Equation of state: \[ P\bar{v} = \bar{R}T \]

\([ \bar{R} = \text{universal gas constant in kJ/kg mol.K} \]
and \( \bar{v} = \text{molar volume in m}^3/\text{kg mol} ] \]

Also: \[ P\bar{v} = RT \]

\([ R = \text{characteristic gas constant in kJ/kg K} ] \]
\( v = \text{specific volume in m}^3/\text{kg} \)

The above equation - Equation of state is also called Characteristic gas equation.

1.24 IDEAL GAS

An ideal gas is a theoretical gas consists of four gas variables i.e., Pressure ($P$), Volume ($V$), Temperature ($T$) and number of mole of a gas ($n$). Lastly, the constant in the equation is $\bar{R}$, which is the universal gas constant ($\bar{R} = 8.314$ kJ/kg mol k)

\[ \bar{PV} = \bar{R}T \]

\( \bar{V} = \text{molar specific volume} \frac{m^3}{\text{kg. mole}} \)

Divide the above equation by molecular weight $\mu$, then the equation becomes,

\[ P\bar{v} = RT \]

where \( \frac{P\bar{v}}{\mu} = RT; R = \frac{\bar{R}}{\mu} \)

\( \mu = \text{molecular weight} \frac{\text{kg}}{\text{mol}} \)
\( R = \text{characteristic gas constant (kJ/kg k)} \)

Also, specific volume, \( v = \frac{\bar{V}}{\mu} \)

Also, \( m = n \mu \)

\( n = \text{number of mole of a gas (kg moles)} \)
\[ m = \text{mass of the gas (kg)} \]

Therefore,

\[ PV = n \bar{R}T \quad \text{(2)} \]

\[ PV = n R \mu T \]

\[ PV = m RT \quad \text{(3)} \]

Equation 1, 2, 3 is called the ideal gas equation of state.

At very low pressure or density, all gases and vapour approaches ideal gas behaviour.

Practically, no ideal gas (perfect gas) exists in nature. However, hydrogen, oxygen, nitrogen and air behave as an ideal gas under normal condition.

Any equation that relates the pressure, temperature and specific volume of a substance is called an **equation of state** which is given here as

\[ PV = RT \]

where the constant of proportionality \( R \) is called the **gas constant**. A gas that obeys this relation is called an ideal gas.

The ideal gas equation is very simple and thus very convenient to use. But, gases deviate from ideal-gas behaviour significantly. This deviation from ideal gas behaviour at a given temperature and pressure can accurately be accounted by the introduction of a correction factor called the **compressibility factor** \( Z \) defined as

\[ Z = \frac{PV}{RT} \quad \text{(or)} \quad PV = ZRT \]

It can also be expressed as

\[ Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}} \quad \text{where} \quad V_{\text{ideal}} = \frac{RT}{P} \]

Obviously, \( Z = 1 \) for ideal gases.

For real gases, \( Z \) can be greater than (or) less than 1 when the gas deviates from ideal - gas behaviour.
A temperature scale which is nearly identical to the Kelvin scale is called ideal gas temperature scale.

Let us suppose a bulb of constant volume gas thermometer which is basically a rigid vessel filled with gas, usually hydrogen or helium at low pressure. Normally, at low pressures. “The temperature of a gas is proportional to its pressure at constant volume”. That is, the pressure of the gas of fixed volume varies linearly with temperature at sufficiently low pressures. Then the relationship between the temperature and the pressure of the gas in the vessel can be expressed as

\[ T = a + bP \]

Where \( a \) and \( b \) are constants for gas thermometers and can be determined experimentally.

An ideal gas temperature scale can be developed by measuring the pressures of the gas in the vessel at two reference points i.e., ice and steam points - considering one straight line passing through fixed points, two equations can be generated which are sufficient to determine the constants \( a \) & \( b \). Now, the unknown temperature can be determined for the given corresponding pressure. The values of the constants will be different for different gas thermometer depending on the type and amount of gas in the vessel. But, if the values of ice and steam points are assigned as 0°C and 100°C, then are gas temperature scale is identical to the celsius scale and the value of constant ‘\( a \)’ is determined as \(-273.15°C\) (corresponds to absolute zero pressure). This value of ‘\( a \)’ remains same for all gas thermometers regardless of the type and amount of gas in the vessel of the gas thermometer.

That is, on a \( P-T \) diagram, all straight lines of different gas thermometers passing through the data points will intersect at \(-273.15°C\). This is the lowest temperature, that can be obtained by any gas thermometer. So we assign the value of ‘\( a \)’ as zero in case of absolute gas temperature scale. Then, the eqn reduces to \( T = bP \) and the temperature can be determined by specifying one fixed point.
It should be noted, that the absolute temperature scale is not a thermodynamic temperature scale, since it cannot measure very low and very high temperatures. It is used in the range in which the gas thermometers can be used and thus the thermodynamic temperature scale can be seen as an absolute temperature scale. (in gas thermometer range) that utilizes ideal gas which always acts as a low pressure gas regardless of the temperature. If such gas thermometer existed, it would read zero kelvin at absolute zero pressure, which corresponds to $-273.15^\circ$C on celsius scale.

The kelvin scale is related to celsius scale by

\[
T (K) = t (^\circ C) + 273.15
\]

### 1.26 CELSIUS TEMPERATURE SCALE

Celsius temperature scale is related to the kelvin scale by

\[ t = T - 273.15 \]

where \( t \) - celsius temperature, \( T \) - kelvin temperature

**eg:** At steam point, \( T = 373.15 \) k i.e., kelvin temperature of steam at 1 atm is 373.15 k

\[ t = 373.15 - 273.15 \]

\[ t = 100^\circ C \]

#### 1.26.1 Contradiction in kelvin scale

The reference point of kelvin scale was changed to the triple point of water in 1954, with the value of 273.16K. The celsius scale was also redefined at the “Tenth General conference on weights and measures” in 1954 in terms of ideal gas temperature scale and single fixed point method, with the triple point of water was found to be 0.01$^\circ$C.

But initially, the reference temperature chosen in the original kelvin scale was 273.15K (0$^\circ$C), which is the temperature at which the water freezes and exists as solid-liquid mixture in equilibrium at standard atmospheric condition.
1.27 GAS THERMOMETERS

There are two main types of gas thermometers and they are:
(i) constant volume gas thermometer
(ii) constant pressure gas thermometer

A simple form of constant-volume gas thermometer is shown in Fig. 1.18. The gas is enclosed in the bulb B and the pressure is recorded by the difference in the levels (h) of the mercury column. The mercury level at R is always adjusted so that it coincides with the mark. The pressure of the gas in the bulb is

\[ P = P_A + P_m \]

where \( P_A \) = Atmospheric pressure \( P_m \) = Manometric pressure

\[ P = P_A + P_m gh_m \]

\( P_m \) - density of mercury; \( h_m \) - height of mercury in liquid column

So, when the bulb is brought in contact with the system, whose temperature is to be measured, the bulb in course of time comes in thermal equilibrium with the system. The gas in the bulb expands, on being heated pushes the mercury downward. The flexible limb of the manometer is again adjusted after the difference in mercury level is recorded. Now the pressure of the gas can be evaluated.

Since the volume of the trapped gas is constant, then the ideal gas equation is,

\[ \Delta T = \frac{V}{R} \Delta P \]

i.e., temperature is directly proportional to pressure.

Similarly, for constant pressure gas thermometer,

\[ \Delta T = \frac{P}{R} \Delta V \]

temperature increases as a result of increase in volume.
1.28 THERMOCOUPLE

Thermocouple is a sensor, which is used to measure temperature. The working principle of thermocouple is based on seebeck effect.

**Seebeck effect**

In 1821, Thomas seebeck discovered that, if metals of two different materials were joined at both ends and if one end was at a different temperature than the other end, a voltage difference between two materials was produced. Thus, a current was created. This phenomenon is known as the seebeck effect and it is the basis for all thermocouples.

The joined ends of thermocouple are referred as hot junction and cold junction. The hot junction is the one where we measure the temperature & cold junction is the other where we connect the measurement instrument.

Due to the seebeck effect, a small voltage is created because of the temperature difference. This voltage is referred to as an EMF (electro motive force).

The voltage created by the thermocouple is extremely small & measured in terms of millivolt (one thousands of a volt).

Various combination of materials are used to makeup the thermocouple pairs. A thermocouple is normally calibrated by measuring the thermal emf at various known temperatures with the reference junction being kept at 0°C. The results of such measurements can usually be represented by a cubic equation of the form.

\[ \varepsilon = a + bt + c t^2 + d t^3 \]
where \( e \) - thermal emf

\( a, b, c, d \) values are different for each thermocouple

**Advantages:**

Thermocouple comes in thermal equilibrium with the system rapidly, because of its lesser mass.

### 1.29 RESISTANCE THERMOMETERS

Resistance thermometers, are also called as resistance temperature detectors (RTDs), are sensors used to measure temperature by correlating the resistance of the thermometer element with the temperature. Most commonly used resistance thermometers are called platinum resistance thermometer (PRT).

PRT measures temperature by a piece of pure platinum wire. The piece of platinum wire is referred to as a temperature sensor. This thermometer measures temperature to a high degree of accuracy and sensitivity, which makes it suitable as a standard for the calibration of other thermometers.

For smaller resistance, the following quadratic equation can be used

\[
R = R_o (1 + At + Bt^2)
\]

where

- \( R_o \) = Resistance of the platinum wire at 0°C (when it is surrounding by melting ice)
- \( A, B \) = constants
- \( t \) = unknown temperature; \( R \) = known resistance

**Solved Problems**

**Problem 1.1:** The emf of the thermocouple with the hot junction \( t \)°C on gas thermometer scale and cold junction at ice point is given by

\[
e = 0.256 - 4 \times 10^{-4} t^2 \text{ mV}
\]

The millivoltmeter is calibrated at ice and steam points. What this thermometer read in a plate where the gas thermometer reads 50°C

At ice point, \( t = 0\)°C, \( e = 0 \)

At steam point

\( t = 100\)°C, \( e = 0.25 \times 100 - 4 \times 10^{-4} (100)^2 = 21 \text{ mV} \)

At 50°C, \( e = 0.25 \times 50 - 4 \times 10^{-4} (50)^2 = 12.5 - 1 = 11.5 \text{ mV} \)
So, when the gas thermometer reads 50°C, the thermocouple will read,

\[ \frac{100}{21} \times 11.5 = 54.76^\circ C \]

**Problem 1.2:** A platinum resistance thermometer has a resistance of 2.5 ohm at 0°C and 3.5 ohm at 100°C. Calculate the temperature when the resistance indicated is 5.5 ohm.

**Given:**

\[ R \text{ at } 0^\circ C = 2.5 \text{ ohm}; \quad R \text{ at } 100^\circ C = 3.5 \text{ ohm} \]

Let \( R = R_0 (1 + \alpha t), R_0 = 2.5 \text{ ohm} \)

\[ R_{100} = R_0 (1 + \alpha 100) \]

\[ \frac{3.5}{2.5} - 1 = 100 \alpha \Rightarrow 0.4 = 100 \alpha \Rightarrow \alpha = 0.4 \times 10^{-2} \]

when \( R = 5.5 \) ohm

\[ 5.5 = 2.5 (1 + (0.4 \times 10^{-2}) t) \]

\[ \frac{5.5}{2.5} - 1 = 0.4 \times 10^{-2} t \Rightarrow 1.2 = 0.4 \times 10^{-2} t \]

\[ t = 300^\circ C \]

Platinum resistance thermometer shows 5.50 ohm at 300 °C

**Problem 1.3:** The temperature \( t \) on a thermometric scale is defined in terms of a property \( k \) by the relation

\[ t = a \ln k + b \]

where \( a \) and \( b \) are constants.

The value of \( k \) are found to be 1.83 and 6.78 at the point (0°C) and steam point (100°C). Determine the temperature corresponding to a reading of \( k \) equal to 2.42 on thermometer.

**Given:**

\[ k = 1.83 \text{ when } t = 0; \quad k = 6.78 \text{ when } t = 100 \quad k = 2.42 \text{ when } t = ? \quad t = a \ln k + b \]

(i) \[ 0 = a \ln (1.83) + b \]

\[ 0.6043 a + b = 0 \]

...(1)
(ii) \[100 = a \ln(6.78) + b\]
\[1.914 a + b = 100\] ...(2)

on solving, \[a = 76.35\] \[b = -46.14\]

(iii) \[t = 76.35 \ln(2.42) - 46.14\]
\[(76.35 \times 0.8838) - 46.14 = t\]
\[t = 21.335^\circ C\]

Problem 1.4: A New scale \(N\) of temperature is divided in such a way that the freezing point of ice is \(100^\circ\)N and the boiling point \(400^\circ\)N what is the temperature reading on the new scale when the temperature in the celsius scale is \(150^\circ\)C. At what temp both the celsius and New temperature scale would be same.

Given:

New temperature scale  
Celsius scale  
Ice point = \(100^\circ\)N  
0\(^\circ\)C  
Boiling point = \(400^\circ\)N  
100\(^\circ\)C  
temperature = ? when 150\(^\circ\)C

Let us take celsius scale on the \(x\) - axis and new temperature scale on the \(y\) - axis

Slope, \[m = \frac{\Delta y}{\Delta x} = \frac{\Delta N}{\Delta C}\]
\[= \frac{400 - 100}{100 - 0}\]
\[= \frac{300}{100} = 3\]

Slope-intercept form equation, is
\[y = mx + b\]  
\[N = mc + b\]
\[N = 3C + 100\] (\(N = 100\) when \(C = 0\))
Temperature on the new scale, when temp or celsius scale is 150°C
\[ N = 3 \times 150 + 100 = 550^\circ N \]
Also, the temp at which both scale readings are same.
At particular temperature, \( N = C \)
From the relation \( N = 3C + 100 \)
\[ C = 3C + 100 \]
\[ C - 3C = 100 \Rightarrow -2C = 100 \]
\[ C = -50^\circ C \text{ (or) } N = -50^\circ N \]
So, at \(-50^\circ\) both the scale would read the same value.

1.30 ENERGY

Energy is the ability of the physical system to perform work. Energy exists in several form such as heat energy, kinetic energy, potential energy, light energy, electrical energy, thermal energy and so on. However, these energy transformations are constrained by a fundamental principle known as the “Conservation of Energy”, Principle. One way to state this principle is “Energy can neither be created nor destroyed, but may transform from one form into another form”.

Another approach is that, “the total energy of the isolated system remains constant”.

In S.I units, energy is represented as Joules (J)

1 Joule = 1 Nm = \( \frac{kg \cdot m}{s^2} \cdot m = \frac{kg \cdot m^2}{s^2} \)

Some forms of energy are explained as follows.

1.30.1 Different forms of energy


1. Potential Energy: (P.E)

It is the energy possessed by any system (or body) by virtue of its height (by virtue of its position above the ground level).

\[ P.E = mg \cdot Z \text{ (or) } mgh \] in J
where \( Z = \) ht above ground level.

\[ P.E = gZ \text{ in J/kg} \]
2. **Kinetic Energy: (K.E)**

   It is the energy possessed by any system (or body) by virtue of its velocity.

   \[ \text{K.E} = \frac{1}{2} \, m \, v^2 \, \text{in J} = \frac{1}{2} \, m \, C^2 \, \text{in J} \]

   where \( v \) = Velocity in m/sec.

   \[ \text{K.E} = \frac{1}{2} \, m \, v^2 \, \text{in J/kg} = \frac{1}{2} \, C^2 \, \text{in J/Kg} \]

   To differentiate from volume \( V \), Velocity ‘\( V \)’ can be denoted by ‘\( C \)’ also.

3. **Pressure Energy**

   It is the energy possessed by any system (or body) by virtue of its pressure.

   \[ \text{Pressure energy} = P \, v = \frac{N \, m^3}{m^2 \, \text{kg}} = \frac{N \, m}{kg} = \text{J/kg} \]

   Sp. pressure energy = \( P \, v \) in J/kg

4. **Internal Energy: (\( u \)) in J**

   It is the energy possessed by any system (or body) due to its molecular arrangement and motion of molecules. ‘\( u \)’ is the specific internal energy in J/kg.

---

### 1.31 WORK

In mechanics

\[ \text{Work} = \text{Force} \times \text{distance moved} = F \times x \]

In thermodynamics, work is said to be done by a system, if sole effect on thing’s external to system can be reduced to the raising of weight.

The weight need not be raised. But the net effect can be utilized to raise the weight Refer **Fig 1.15**.

Let \( A \) = Cross sectional area of the piston in m\(^2\)

\[ P = \text{Pressure of gas at any time} \]

---

**Fig. 1.20**
\( dl \) = Distance moved by the piston under gas pressure.

Work done = Force \times distance travelled
\[ = (PA) \times dl \]
\[ = P(Adl) = Pdv \]

Consider unit mass.

Then \( W = Pdv \) [where \( v \) = specific volume]

When the reversible process (Quasi-static process) takes place between states 1 and 2, then

\[ \text{Work done} = \int_{1}^{2} Pdv \]

Therefore the work done by the gas during any reversible process is given by the area under the \( Pv \) diagram. (Shaded area).

When the work is done by the system, it is positive work \( \text{Fig 1.21(a)} \).

When the work is done on the system, it is negative work \( \text{Fig 1.21(b)} \).

1.32 WORK TRANSFER - A PATH FUNCTION

Let us consider a system shown in \( \text{Fig 1.22} \).

The system moves from an equilibrium state 1 to a final equilibrium state 2 through two different paths \( 1 \rightarrow A \rightarrow 2 \) and \( 1 \rightarrow B \rightarrow 2 \). The processes are quasi-static.

Since area under each curve represents the work for each process. \( 1 \rightarrow A \rightarrow 2 \) gives one value of work and \( 1 \rightarrow B \rightarrow 2 \) gives another value of work. So
the work does not depend on the end state of the process. But it depends on the path the system it follows. So the work is called path function. Hence $\,\,dW$ is an **inexact or imperfect differential**.

$$W_2 - W_1 = \int_1^2 dW = \int_1^2 Pdv$$

**Note:**

*Thermodynamic properties are point functions, since they depend only on the end states.*

Example: Change in volume $= V_2 - V_1$

Change in pressure $= P_2 - P_1$ Change in temperature $= t_2 - t_1$

So the properties of the system depend on only end states and independent of the path the system follows. So the differentiation of point functions are **exact** or **perfect** differentials.

**Note:**

For a cyclic process, the initial and final states of the system are the same, and hence, the change in any property is zero.

$$\oint dV = 0, \oint dP = 0, \oint dT = 0$$

where the sign $\oint$ denotes the cyclic integral for the closed path. Therefore, cyclic integral of a property is always zero.

**1.33 DIFFERENT MODES OF WORK**

**1.33.1 Electrical work**

When a current flows through a resistor (as shown in Fig. 1.23) taken as a system there is work transfer into the system. This is because the current can drive a motor, the motor can drive a pulley and the pulley can rise a weight.

The electrons crossing the system boundary do electrical work on the system. In an electrical field, electrons in a wire move under the effect of electromotive forces, doing work.
When current $I$ flows through a potential difference $V$, the electrical work done in the rate form is $We = VI$

where $We$ is the electrical power. In general, both $V$ and $I$ vary with time, and the electrical work done during a time interval $\Delta t$ is given by

$$We = \int_1^2 VI \, dt \text{ (kJ)}$$

### 1.3.3.2 Shaft Work

Since the torque applied to the shaft is constant, the force $F$ applied is also constant (Fig 1.24).

Because Torque

$$T = \text{Force (F)} \times \text{radius (r)}$$

$$T = F \times r$$

For a specified constant torque $T$, the work done during $n$ revolutions is determined as follows.

We know $T = F \times r \quad \text{(or)} \quad F = \frac{T}{r}$

This force acts through a distance $s$, which is related to the radius $r$ by

$$s = (2\pi r) n$$

Then the shaft work is determined from

$$W_{sh} = Fs = \left(\frac{T}{r}\right) (2\pi r n) = 2\pi n T \text{ kJ}$$

Also it can be given as $W_{sh} = \int_1^2 T \, d\theta \text{ kJ}$ where $d\theta$ is the angular displacement the shaft.

The power transmitted through the shaft is the shaft work done per unit time which can be given as

$$\dot{W}_{sh} = \frac{2\pi NT}{60 \times 1000} \text{ kW}$$

where $N = \text{Number of revolutions per minute}$
Power Transmission by the shaft of a car.

**Problem 1.5:** Determine the power transmitted through the shaft of a car when the torque applied is 300 N-m and the shaft rotates at a rate of 3500 revolutions per minute (rpm).

**Solution:**

We know

\[ \dot{W}_{sh} = \frac{2\pi N T}{60} \]

\[ = 2\pi \left( \frac{3500}{60} \right) \times \frac{300}{1000} = 109.96 \text{ kW} \]

**1.33.3 Spring Work**

When a force is applied on a spring, the length of the spring changes. Refer Fig. 1.25 and Fig. 1.26. When the length of the spring changes by a differential amount \( dx \) under the influence of a force \( F \), the work done is

\[ \delta W_{spring} = F \, dx \]

To determine the total spring work, it is necessary to know the linear relationship between \( F \) and \( x \). For linear elastic springs, the displacement \( x \) is proportional to the force applied, i.e

\[ F = kx, \text{ where } k = \text{ spring constant in kN/m} \]

To get the total spring work

\[ \delta W_{spring} = F \, dx \Rightarrow F = kx \]

\[ \delta W_{spring} = kx \cdot dx \]
Integrating
\[ \int_{1}^{2} \delta W_{\text{spring}} = \int_{1}^{2} kx \, dx \]

\[ W_{1-2} = \frac{1}{2} k (x_2^2 - x_1^2) \text{ kJ} \]

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

**Expansion of a Gas against a spring.**

**Problem 1.6:** A piston-cylinder device contains 0.05 m\(^3\) of a gas initially at 200 MPa. At this state, a linear spring that has spring constant of 150 kN/m is touching the piston but exerting no force on it. Now heat is transferred to the gas, causing the piston to rise and compress the spring until the volume inside the cylinder doubles. If the cross sectional area of the piston is 0.25 m\(^2\), determine the fraction of work done by the gas against the spring to compress it.

**Solution**

**Assumptions:** The expansion process is quasi-equilibrium

The spring is linear in the range of interest.

The enclosed volume at the final state is

\[ V_2 = 2V_1 = 2 \times 0.05 = 0.1 \text{ m}^3 \]

Then the displacement of the piston (and of the spring) becomes

\[ x = \frac{\Delta V}{A} = \frac{(0.1 - 0.05)}{0.25} = 0.2 \text{ m} \]

We know,

\[ W_{\text{spring}} = \frac{1}{2} k \left( x_2^2 - x_1^2 \right) \]

Here final displacement \( x_2 = 0.2m \)

Initial displacement \( x_1 = 0 \)

\[ W_{\text{spring}} = \frac{1}{2} \times 150 \times (0.2^2 - 0^2) = 3 \text{ kJ} \]
### 1.33.4 Paddle wheel work (or) Stirring work

When the weight is lowered, and the paddle wheel turns, there is work transfer into the fluid system which gets stirred. Since the volume of the system remains constant,

\[ \int PdV = 0 \]

But work done \( dW = mg \, dz \), where \( m = \) mass of weight lowered.

This work can be equated as, \( mg \, dz = Td \theta \)

To find total work transfer

\[ W = \int_{1}^{2} mg \, dz = \int_{1}^{0} Td \theta \]

### 1.33.5 Flow Work

The flow work occurs only in flow process (or) open system. Unlike the closed systems, control volume involve mass flow across their boundaries, and some work is required to push the mass into (or) out of the control volume. This work is known as the **flow work** (or) **flow energy**, and is necessary for maintaining a continuous flow through a control volume.

Refer the **Fig. 1.27 a and 1.27 b**

Consider a fluid element of volume \( V \) as shown in fig. The fluid immediately upstream will force this fluid element to enter the control volume. Thus, it can be regarded as an imaginary piston.

When the fluid pressure \( P \) and the cross sectional area of the fluid element is \( A \), the force applied on the fluid element by the imaginary piston is

\[ F = PA \]

To push the entire fluid element into the control volume, the force must act through a distance \( L \). Thus, the
The work done in pushing the fluid element across the boundary (i.e., the flow work) is

\[ W_{\text{flow}} = FL = PAL = PV \text{ (kJ)} \]

The flow work per unit mass is obtained by dividing both sides of this equation by the mass of the fluid element:

\[ W_{\text{flow}} = PV \text{ (kJ/kg)} \]

The flow work relation is the same whether the fluid is pushed into (or) out of the control volume.

### 1.33.6 Workdone on Elastic solid bars

Solids are considered as linear springs because under the action of a force, they contract (or) elongate as shown in Fig. 1.28, and when the force is removed, they return to their original lengths, like a spring. This is true as long as the force is in the elastic range, that is, not large enough to cause permanent (plastic) deformations. Therefore, the equations given for a linear spring can also be used for elastic solid bars.

We can determine the work associated with the expansion (or) contraction of an elastic solid bar by replacing \( P \) by \( \sigma_n \).

Normal stress \( \sigma_n = \frac{F}{A} \)

Hence \( W_{\text{elastic}} = \int_{1}^{2} \sigma_n \, dV \)

\[ = \int_{1}^{2} \sigma_n \, A \, dx \text{ (kJ)} \]

where \( A \) is the cross-sectional area of the bar. Note that the normal stress has pressure units.

### 1.33.7 Work Associated with the stretching of a Liquid Film

Refer the Fig. 1.29

Consider a liquid film such as soap film suspended on a wire frame. Some force is needed to stretch this film by the movable portion of the wire frame. This force is used to overcome the microscopic forces between molecules at the liquid-air interfaces.
These microscopic forces are perpendicular to any line in the surface and the force generated per unit length is called the \textbf{surface tension} $\sigma_s$, where unit is N/m. Therefore, the work associated with the stretching of a film is also called \textbf{surface tension work}.

It is determined from,

$$W_{\text{surface}} = \int_1^2 \sigma_s dA \text{ (kJ)}$$

where $dA = 2bdx$ is the change in the surface area of the film. The factor 2 is due to the fact that the film has two surfaces in contact with air.

\textbf{1.33.8 Workdone per unit volume on a magnetic material}

$$dW = Hdl$$

$$W_{1-2} = \int_1^2 Hdl \text{ (kJ)}$$

where $H$ is the field strength and $I$ is the component of the magnetization field in the direction of the field.

\textit{The following equations summarize the different modes of work transfer.}

- Electrical work : $W_e = \int_1^2 VI \, dt \text{ (kJ)}$
- Shaft work : $W_{\text{shaft}} = \int_1^2 Td\theta \text{ (kJ)}$
- Spring work : $W_{\text{spring}} = \int_1^2 kx \, dx \text{ (kJ)}$
Elastic solid bar: \( W_{\text{elastic}} = \int_{1}^{2} \sigma_n A \, dx \) (kJ)

Surface Film: \( W = \int_{1}^{2} \sigma_d A \) (kJ)

Magnetic solid: \( W = \int_{1}^{2} H dI \)

Apart from the above, a very important work transfer is Displacement work for compressible fluid \( \int Pdv \) work. Which will be explained later in this book.

1.34 FREE EXPANSION WORK

Work transfer is a boundary phenomenon and can be identified only at the system boundaries. It is a form of energy in transit crossing the boundary. Let us, consider a gas separated from the vacuum by a partition as shown in Fig. Now, let the partition be removed. The gas expands inside the chamber to fill the entire volume. This expansion of a gas against vacuum is called as free expansion.

Suppose, if we neglect the work involved with the removal of partition, and also consider gas and vacuum as a system, then there is no work transfer associated here, since no work crosses the boundary.

So,

\[
\int_{1}^{2} dw = 0
\]

But, if the gas alone is taken as a system as shown in Fig.1.30 (b), then the gas is initially confined to a volume \( V_1 \), pressure \( P_1 \) and temperature \( T_1 \). And, after expansion, the gas takes Volume \( V_2 \), Pressure \( P_2 \) and temperature \( T_2 \).

Now, the work transfer can be calculated from the relation
Since the initial and final states are in equilibrium, the two end states can be located on the $P-V$ diagram as a dotted line.

But, if the vacuum space is divided into large no. of small partitions and the partitions are removed one by one, then every state passed by the system is an equilibrium state & the work done can be estimated along with the $P-V$ diagram.

Besides these, however, in free expansion of a gas, there is no resistance to the fluid at the system boundary. Since vacuum does not offer any resistance, there is no work transfer involved in free expansion.

### 1.35 HEAT

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

The transfer of heat between two bodies in contact is called **conduction**. The transfer of heat between a wall and a fluid system in motion is called **convection**. The transfer of heat between two bodies separated by empty space (or) gases through electromagnetic waves is called **radiation**.
The temperature difference is the driving force for heat transfer. The larger the temperature difference, the higher is the rate of heat transfer. Refer Fig 1.31.

Normally, the heat is transferred from high temperature system to the low temperature system. The transfer of heat into a system is frequently referred to as heat addition and is taken as positive. The transfer of heat out of a system is called heat rejection and is taken as negative.

Refer Fig. 1.32. A process during which there is no heat transfer is called an adiabatic process. An adiabatic process should not be confused with an isothermal process. Even though there is no heat transfer during an adiabatic process, the energy content and thus the temperature of a system can still be changed by other means such as work.

As a form of energy, heat has energy units, kJ. The amount of heat transferred during the process between two states (states 1 and 2) is denoted by \( Q_{1-2} \). Heat transfer per unit mass of a system is denoted by \( q \).

\[
q = \frac{Q}{m} \text{ (kJ/kg)}
\]

The rate of heat transfer is the amount of heat transferred per unit time is denoted by \( \dot{Q} \), where the overdot stands for the unit derivative (or) “per unit time”. The heat transfer rate \( \dot{Q} \) has the unit kJ/s, which is equivalent to kW.
1.35.1 Heat Transfer – A Path Function

Heat transfer is also a path function. It depends on the path the system follows. It does not depend on the end states. So $\delta Q$ is inexact differential.

Refer Fig. 1.34. Area under $T$-$S$ diagram gives the heat transfer. In the processes $A$ and $B$, the end states are same, but the path are different. So the heat transfers in two processes $A$ and $B$ are different.

$$Q_{1-2} = \int_1^2 \delta Q = \int_1^2 Tds$$


Note

$W_{1-2} \neq W_1 - W_2$: $W_{1-2}$ = Work transfer from 1 to 2.

$Q_{1-2} \neq Q_1 - Q_2$: $Q_{1-2}$ = Heat transfer from 1 to 2.

$s = \text{entropy (which will be explained later).}$

$ds = \text{change in entropy.}$

Path functions have Inexact differentials designated by the symbol $\delta \ (or) \ d$. Therefore, a differential amount of heat (or) work is represented by $\delta Q \ or \ dQ, \delta W \ or \ dW$, respectively, instead of $dQ \ (or) \ dW$. 

![Fig. 1.34](image_url)
1.36 HEAT CAPACITY

Heat capacity (also called as the thermal capacity is the ratio of the heat added to (or) heat removed from an object to the resulting temperature change.

It can also be defined as a product of mass and specific heat.

\[ C = mc \]

\[ = \text{kg} \times \frac{\text{J}}{\text{kgK}} = \frac{\text{J}}{\text{K}} \]

It is denoted by capital letter \((C, C_p, C_v)\)

The S.I unit of heat capacity is Joule/Kelvin.

1.37 REVERSIBLE AND IRREVERSIBLE PROCESS

Reversible process
A process in which both system and its surroundings can be simultaneously returned to their initial states after the process has been completed.

Irreversible process
A process in which both system and its surroundings cannot be simultaneously returned to their initial states after the process has been completed.

<table>
<thead>
<tr>
<th>Reversible process</th>
<th>Irreversible process</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Reversible process is an ideal process</td>
<td>Irreversible process is a natural process. (i.e.) all the processes occurring in nature are irreversible.</td>
</tr>
<tr>
<td>(ii) Reversible process attains equilibrium state at all the stages of the operation.</td>
<td>Irreversible process is in equilibrium only at the initial and final stages of operation.</td>
</tr>
<tr>
<td>(iii) It is a extremely slow process.</td>
<td>It occurs at measurable speed.</td>
</tr>
<tr>
<td>(iv) It takes infinite time for the process to occur.</td>
<td>It takes place in finite time.</td>
</tr>
<tr>
<td>(v) Workdone by a reversible process is greater than the corresponding irreversible process.</td>
<td>Workdone by an irreversible process is lesser than the corresponding reversible process.</td>
</tr>
<tr>
<td>(vi) It does not increase the entropy of the universe.</td>
<td>It increases the entropy of the universe (system &amp; surroundings).</td>
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</tbody>
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