TOPIC: Basic Concepts of Thermodynamics & Thermodynamics Laws

Instructor: N. S. Sivakumar
Objective

• To Understanding the thermodynamics terms such as system, state, equilibrium, process, cycle, Properties of system and Application of thermodynamics.

In this lecture, deals with thermodynamic properties such as temperature, pressure, density, specific volume, specific gravity.

The concept of Ideal and real gas and Ideal gas laws, thermal equilibrium, heat and work.
Introduction

• Applications: Thermodynamics in Engineering Systems
  • Power Generation
  • Refrigeration and Heat Pumps
  • Internal Combustion Engines
  • HVAC Systems (Heating, Ventilation and Air Conditioning)
  • Jet Propulsion
  • Supersonic Flows
  • Fuel Cells
  • Reacting and non-Reacting Processes
Why do Engineers study Thermodynamics

Thermodynamics is a branch of physics dealing with the relationships between heat and other forms of energy. Engineers study Thermodynamics because it forms the basis for understanding and designing systems that involve heat transfer, energy conversion, and fluid dynamics. This knowledge is crucial for the development of efficient and sustainable technologies in various fields, including energy generation, transportation, and biomedical engineering.
Energy

Energy as a whole WRT some outside reference, and changes with velocity and elevation to a reference.

Macroscopic

Kinetic

\[ KE = \frac{1}{2}mv^2 \]

Potential

\[ PE = mgz \]

Microscopic

Sensible

Sum of translational, vibrational, rotational. Higher at higher temperatures.

Latent

Inter-molecular (phase change)

Chemical

Atomic

Bonds within nucleus of atoms

The summation of all microscopic energies is called internal energy, \( U \).

\[ E = U + KE + PE \quad (kJ) \]
## Comparison of Microscopic and Macroscopic Approach

<table>
<thead>
<tr>
<th>Macroscopic approach</th>
<th>Microscopic approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>In this approach, a certain quantity of matter is considered without taking into account the energy occurring at the molecular level. This is known as <strong>classical Thermodynamics</strong>.</td>
<td>In this approach, the energy occurring at the molecular level is taken into account for analysis. The values of these energies are constantly changing with time. This is known as <strong>statistical Thermodynamics</strong>.</td>
</tr>
<tr>
<td>The analysis of macroscopic systems requires <strong>simple mathematical formulae</strong></td>
<td>The behaviour of the system is found by using <strong>statistical method</strong> as the number of molecules is very large.</td>
</tr>
<tr>
<td>Macroscopic approach</td>
<td>Microscopic approach</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>The values of the properties of system are their <strong>average values</strong>. <strong>Example:</strong> consider a sample of a gas in a closed container. The pressure of the gas is the average value of the pressure exerted by millions of individual molecules.</td>
<td>The properties like velocity, momentum, impulse, kinetic energy, force of impact etc, which describe the molecule cannot be easily measured by instruments. Our senses cannot feel them.</td>
</tr>
<tr>
<td>In order to describe such a system only a <strong>few variables</strong> are needed.</td>
<td><strong>Large number of variables</strong> are needed to describe such a system. So the approach is complicated.</td>
</tr>
</tbody>
</table>
Thermodynamic Systems

• A thermodynamic system is defined as a “Quantity of matter or region in space, or area chosen for study of energy transfer and conversions.
**SYSTEM**: Quantity of matter or region in space, chosen for study.

**SURROUNDINGS**: Mass or region outside the SYSTEM.

**BOUNDARY**: Real / Imaginary surface that separates the SYSTEM from SURROUNDINGS.

- **Fixed / Movable**
- **Shared by both, SYSTEM and SURROUNDINGS**
- **No Thickness**
- **No Mass / Volume**
Closed System

Also known as **CONTROL MASS**
Example of a closed system – a pressure cooker.
Also known as **CONTROL VOLUME**

example, boiling water without a lid
Isolated System

This system has no mass and Energy interactions. This system is completely sealed.

Example: Entire Universe and Thermo Flask

**Adiabatic system**
Any characteristic of a System is known as its **PROPERTY**.

- e.g. Pressure (P), Volume (V), Temperature (T) and mass (m), etc.
- also Viscosity (\(\mu\)), Electric Resistance (R), Thermal Conductivity (\(k\)), etc.

**Intensive** : **Independent** on mass of system.
- e.g. pressure, temperature, specific volume and density etc.

**Extensive** : **Dependent** on mass of system.
- e.g. mass, volume, total energy, weight, etc.
Temperature

TEMPERATURE:

- No EXACT Definition.

- Broad Definition: “Degree of Hotness / Cold”

- This definition is based on our physiological sensation.

- Properties of materials change with temperature.

- We can make use of this phenomenon to deduce EXACT level of temperature.
Temperature Scales

1. Celsius Scale (°C) – SI System
2. Fahrenheit Scale (°F) – English System
3. Kelvin Scale (K) – SI System
4. Rankine Scale (R) – English System

Celsius Scale and Fahrenheit Scale – Based on 2 easily reproducible fixed states, viz. Freezing and Boiling points of water.

i.e. Ice Point and Steam Point

Thermodynamic Temperature Scale – Independent of properties of any substance.

- In conjunction with Second Law of Thermodynamics

Thermodynamic Temperature Scale – Kelvin Scale and Rankine Scale.
Temperature Scales

Conversion Factors:

\[
\begin{align*}
T(K) &= T(\degree C) + 273.15 \\
T(R) &= T(\degree F) + 459.67 \\
T(\degree F) &= 1.8T(\degree C) + 32 \\
T(R) &= 1.8T(K) - 273.15
\end{align*}
\]
Pressure and its Units

Definition: Normal Force exerted by a fluid per unit Area.

SI Units:

1 Pa = 1 N/m²
1 kPa = 10³ Pa
1 MPa = 10⁶ Pa = 10³ kPa
1 bar = 10⁵ Pa = 0.1 MPa = 100 kPa = 100 N/m²
1 atm = 101325 Pa = 101.325 kPa = 1.01325 bar
1 kgf/cm² = 9.81 N/m² = 9.81 x 10⁴ N/m² = 0.981 bar = 0.9679 atm

English Units:

psi = Pound per square inch ( lbf/in²)
1 atm = 14.696 psi
1 kgf/cm² = 14.223 psi
Types of Pressure

**Absolute Pressure**: Actual Pressure at a given position. Measured relative to absolute vacuum i.e. absolute zero pressure.

Pressure Gauges are generally designed to indicate **ZERO** at local atmospheric pressure.

Hence, the difference is known as **Gauge Pressure**.

i.e. \( P \text{(gauge)} = P \text{(abs)} - P \text{(atm)} \)

Pressure less than local atmospheric pressure is known as **Vacuum Pressure**.

i.e. \( P \text{(vacuum)} = P \text{(atm)} - P \text{(abs)} \)
Local Atmospheric Pressure (1.01325 bar @ Sea Level)

Absolute Zero Pressure

\[ P_{\text{gauge}} = P_{\text{abs}} - P_{\text{atm}} \]

\[ P_{\text{vacuum}} = P_{\text{atm}} - P_{\text{abs}} \]
Density

• **Density** is defined as mass \( \rho = \frac{m}{V} \) (kg/m\(^3\))

• The density of a quantity of matter is defined as:

\[ \rho = \lim_{V \to V'} \left( \frac{m}{V} \right) \]

• \( V' \) is the smallest volume containing enough particles such that statistical averages are significant. It is also the smallest volume that we can consider the region a “point” and still maintain the continuum hypothesis.

• Density can vary from point to point within the system.
Specific Volume and Specific Gravity

• The reciprocal of density is the specific volume $v$, which is defined as volume per unit mass. That is,

$$v = \frac{V}{m} = \frac{1}{\rho}$$

• Sometimes the density of a substance is given relative to the density of a well-known substance. Then it is called specific gravity, or relative density, and is defined as the ratio of the density of a substance to the density of some standard substance at a specified temperature (usually water at 4°C, for which $\rho_{H_2O} = 1000 \text{ kg/m}^3$).

$$SG = \frac{\rho}{\rho_{H_2O}}$$
Assume a System **NOT** undergoing any change.

Set of properties to completely describe the condition of the system is known as **STATE**
EQUILIBRIUM : State of Balance

Thermal Equilibrium :
- NO Temperature Gradient throughout the system.

Mechanical Equilibrium :
- NO Pressure Gradient throughout the system.

Phase Equilibrium :
- System having more than 1 phase.
- Mass of each phase is in equilibrium.

Chemical Equilibrium :
- Chemical composition is constant
- NO reaction occurs.
Any changes in a system undergoes from one equilibrium state to another is known as PROCESS.

Series of states through which system passes during the process is known as its PATH.
Thermodynamics

Path & Process

Pressure (P) vs Volume (V)

- Volume = Constant (Isochoric)
- Pressure = Constant (Isobaric)
A system is said to have undergone a cycle if it returns to its ORIGINAL state at the end of the process.

Hence, for a CYCLE, the INITIAL and the FINAL states are identical.
Reversible / Irreversible Process

**Reversible Process**: Process that can be reversed without leaving any trace on the Surroundings. i.e. Both, System and Surroundings are returned to their initial states at the end of the Process. This is only possible when net Heat and net Work Exchange between the system and the surroundings is **ZERO** for the Process.

Pendulum

Quasi-Static Compression and Expansion
Most of the Processes in nature are **IRREVERSIBLE**.

i.e. Having taken place, they **can not** reverse themselves spontaneously and restore the System to its original State.

**e.g.** Hot cup of coffee → Cools down when exposed to Surroundings.

But, → Warm up by gaining heat from Surroundings.

i.e. w/o external Heat supply.
Reversible / Irreversible Process

Why REVERSIBLE Process?

1. Easy to analyse, as System passes through series of Equilibriums.
2. Serve as Idealised Model for actual Processes to be compared for analysis.
3. Viewed as Theoretical Limit for corresponding irreversible one.

Reversible Process leads to the definition of Second Law Efficiency; which is Degree of Approximation (Closeness) to the corresponding Reversible Process.

(↑) Better the Design, (↓) Lower the Irreversibilities; (↑) Second Law Efficiency.
• Ideal Gas
  • An ideal or perfect gas is one whose pressure, volume, and temperature are related by the ideal gas law. It is an imaginary substance.

• Real Gas
  • A real gas is a gas that does not behave as an ideal gas due to interactions between gas molecules. A real gas is also known as a nonideal gas because the behavior of a real gas in only approximated by the ideal gas law.
The ideal gas law states that the pressure, temperature, and volume of gas are related to each other. The following equation can be used to express the relationship:

\[ PV = mRT \]

or

\[ PV = nRT \]

where \( P \) is the pressure measured in atmospheres or mmHg or Pa (=N m\(^{-2}\)), or some other appropriate unit, \( V \) is the volume, \( n/m \) is the number of moles/mass, \( R \) is the gas constant, and \( T \) is the temperature in kelvin.
Boyles Law

Pressure of the gas is inversely proportional to its Volume.

PV = Constant

or

P ∝ 1/V
Charles Law

Volume of the gas is directly proportional to its Temperature.

\[ \frac{V}{T} = \text{Constant} \]

OR

\[ V \propto T \]
Gay-Lussac Law

Pressure of the gas is directly proportional to its Temperature.

\[
P / T = \text{Constant} \quad \text{or} \quad P \propto T
\]
Ideal OR Characteristic Gas Equation

R is the Constant of Proportionality, given by the unit (kJ/kg.K)
R=0.287 kJ/kg.K (For Air)

Now, \( V \) (Total Volume) = \( m \cdot v \) (Sp. Vol.)

\[ PV = mRT \]

Thus, for a fixed mass;

\[ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \]

Behaviour of a Real Gas approaches to the that of an Ideal Gas, at low densities.

Thus, at low pressures and high temperatures, the density of the gas decreases and the gas approaches to Ideal Gas.
Thermal Equilibrium:

- **Thermal Equilibrium**: NO change w.r.t. Temperature
- NO Temperature Gradient.

HOT cup of tea / coffee cools off w.r.t. time.

COLD Drink warms up w.r.t. time.

When a body is brought in contact with another body at different temperature, heat is transferred from the body at higher temperature to that with lower one; till both attain a THERMAL EQUILIBRIUM.
Energy can cross the Boundary of the System in 2 forms: 1. Heat

Heat & Work

Energy can cross the Boundary of the System in 2 forms: 1. Heat

Heat is a form of Energy transferred between 2 Systems (or a System and the surroundings) by virtue of Temperature Difference (ΔT).

i.e. Heat is Energy in TRANSITION.

Process involving no Heat Exchange is known as ADIABATIC Process.

Heat, Q = 0

Adiabatic

Atmosphere 25°C

Q = 0

Heat, Q

15°C
Heat & Work

Possibilities of Adiabatic Process:

1. Perfect Insulation: Negligible Energy transfer through Boundary.

2. Both System and Surrounding at same temperature.
   - No Energy transfer due to absence of driving force ($\Delta T$).

**NOTE:** Adiabatic Process ≠ Isothermal Process

- No Heat Transfer
- Energy content & temperature of the system can be changed with help of Work.
Modes of Heat Transfer

CONDUCTION: Transfer of Energy from a more energetic particle of a substance to the adjacent less energetic one, as a result of interaction between them.

CONVECTION: Transfer of Energy between a solid surface and the adjacent fluid that is in motion. It involved both, the combined effect of conduction and fluid motion.

RADIATION: Transfer of Energy due to the emission of electromagnetic waves.
**WORK** : Work is the Energy transfer associated with a Force acting through a distance.

Denoted by J or kJ.

e.g. Raising Piston, Rotating Shaft, etc.
Sign conversions

\[ \text{Sp. Work} = \text{Work per unit Mass} \]
\[ w = \frac{W}{m} \text{ ( J/kg )} \]

\[ \text{Power} = \text{Work per unit Time} \]
\[ P = \frac{W}{\text{time}} \text{ ( J/sec OR W )} \]

**Sign Convention:**

- \( \text{Qin} \)-Heat supplied **TO** a System : + ve
- \( \text{Qout} \)-Heat rejected **BY** a System : - ve
- \( \text{Wout} \)-Work done **BY** a System : + ve
- \( \text{Win} \)-Work done **ON** a System : - ve
Different materials require different amount of Energy for their temperatures to increase thought unit quantity (i.e. 1 °C) for identical mass.

Hence, it is required to define a Property to compare the ENERGY STORAGE CAPACITY of different substances.

This Property is known as SPECIFIC HEAT.

The specific heat of liquid water is 4.184 J/g °C which is also 4.184 KJ/Kg°C.
Specific Heat Capacity (C)

DEFINITION:
The Energy required to raise the temperature of a unit mass of a substance by 1 degree.

Specific Heat at Constant Pressure (Cₚ) :
The Energy required to raise the temperature of a unit mass of a substance by 1 degree, as the Pressure is maintained CONSTANT.

Specific Heat at Constant Volume (Cᵥ) :
The Energy required to raise the temperature of a unit mass of a substance by 1 degree, as the Volume is maintained CONSTANT.
Specific Heat capacity for Air

\[ C_v = 0.718 \text{ kJ/kg.}°\text{C} \]

\[ C_p = 1.005 \text{ kJ/kg.}°\text{C} \]

\( C_p \) is always greater than \( C_v \); as the System is allowed to expand in case of Const. Pr. and the Energy for this expansion Work is also need to be supplied.

NOTE; For Solid and liquid have only one sp.heat capacity. But for gas and vapours have TWO Sp.heat capacities (\( C_p \) and \( C_v \))
Hence, \( C_V \) is change in Internal Energy of a substance per unit change in temperature at constant Volume.

Hence, \( C_P \) is change in Enthalpy of a substance per unit change in temperature at constant Pressure.
\[ h = u + P v \quad \text{....by Definition of Enthalpy} \]

But, \( P v = RT \) \quad \text{....by Ideal Gas Law}

Thus, \( h = u + RT \)

\[ dh = du + R \, dT \]

\[ C_p \, dT = C_v \, dT + R \, dT \quad \text{....by Definition of } C_p \text{ and } C_v \]

\[ C_p = C_v + R \quad (kJ/kg.K) \]

Specific Heat Ratio, \( k \) (or \( \gamma \)) is given by;

\[ k \text{ (or } \gamma \text{ )} = \frac{C_p}{C_v} \]
• Summary

In this lecture, deals with thermodynamic properties such as temperature, pressure, density, specific volume, specific gravity. The concept of Ideal and real gas and Ideal gas laws, thermal equilibrium, heat and work.

Also we discussed about Sp.heat capacities for solid and fluids.

The specific heat capacity, or the amount of heat needed to raise the temperature of a specific substance in a specific form one degree Celsius, for water is 4.187 kJ/kgK, for ice 2.108 kJ/kgK, and for water vapor (steam) 1.996 kJ/kgK.
Summery

• We have learned the thermodynamics terms such as system, state, equilibrium, process, cycle, Properties of system and Application of thermodynamics.

• And also we have discussed about the importance of Reversible and Irreversible Process.
TOPIC: Thermodynamics Laws
(Zeroth, first and second Laws)

2nd Grade - Fall Semester 2020-2021

Instructor: N. S. Sivakumar
Zeroth Law of Thermodynamics

• **Zeroth Law of Thermodynamics**
  • States that when two bodies have equality of temperature with a third body, they in turn have equality of temperature with each other.

• **Why is it the Zeroth Law?**
  • While this principle seems obvious, it is not derivable from other laws, and because it precedes the First and Second laws of thermodynamics in the logical presentation of fundamentals, it has come to be known as the Zeroth Law!
  • This is the *basis for measurement of temperature*. 
Zeroth Law of Thermodynamics

STATEMENT:
If two bodies are in Thermal Equilibrium with the third body, then they are also in Thermal Equilibrium with each other.

This statement seems to be very simple. However, this can not be directly concluded from the other Laws of Thermodynamics. It serves as the basis of validity of TEMPERATURE measurement.
The first law of thermodynamics, also known as Law of Conservation of Energy

• 1\textsuperscript{st} Law of Thermodynamics – Energy cannot be created or destroyed.
  – Energy lost during one process must equal the energy gained during another

First Law of Thermodynamics

• Conservation of energy:
  \[ q = \Delta e + w \]

• The amount of heat (\(q\)) added to a system is equal to the change in internal energy (\(\Delta e\)) of the system plus any work (\(w\)) done by the system
First Law of Thermodynamics

- Conservation of energy:
  \[ q = \Delta e + w \]

- The amount of heat \( (q) \) added to a system is equal to the change in internal energy \( (\Delta e) \) of the system plus any work \( (w) \) done by the system
Second Law of thermodynamics

- 2\textsuperscript{nd} Law of Thermodynamics – Heat can spontaneously flow from a hotter object to a cooler object, but not the other way around.
- The amount of heat lost by the warm object is equivalent to the heat gained by the cooler object.
Second Law of Thermodynamics

This process is **Spontaneous** (occurs on its own). So entropy of the universe increases.

Air leaks from the balloon on its own

This process is **Non-spontaneous** (does not occur on its own). So entropy of the universe decreases.

Air never enters the balloon on its own

*Entropy Statement of Second law of thermodynamics:*

*"In all the spontaneous processes, the entropy of the universe increases."*

Let me explain this to you.

The air from the balloon leaks on its own, while the reverse process is not
Summary

First law of thermodynamics is quantitative. It just states that energy can neither be created nor be destroyed but it can be converted from one form to another.
While second law of thermodynamics is qualitative law. It deals with the entropy and irreversibility of the system. We can determine whether the process is naturally feasible or not.
Again there is one more point to be noted is that, heat is low grade energy and work is high grade energy. We can't covert heat into work completely. But we can convert work into heat completely.
Summary

The Laws of Thermodynamics

0. Two bodies in thermal equilibrium are at same T
1. Energy can never be created or destroyed.
   \[ \Delta E = q + w \]
2. The total entropy of the UNIVERSE
   ( = system plus surroundings) MUST INCREASE
   in every spontaneous process.
   \[ \Delta S_{\text{TOTAL}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]
3. The entropy (S) of a pure, perfectly crystalline
   compound at T = 0 K is ZERO. (no disorder)
   \[ S_{T=0} = 0 \text{ (perfect xll)} \]