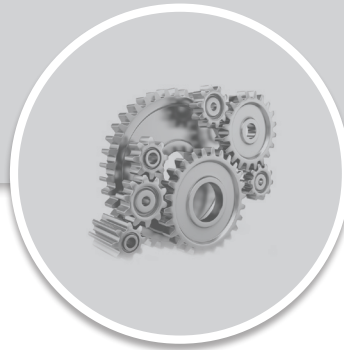


MECHANICAL ENGINEERING

Thermodynamics



Comprehensive Theory
with Solved Examples and Practice Questions





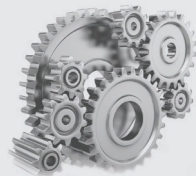
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Thermodynamics

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CONTENTS

Thermodynamics

CHAPTER 1

Basic Concepts & Zeroth Law of Thermodynamics 1-14

1.1	Introduction	1
1.2	Systems, Surroundings and Boundary.....	2
1.3	Homogeneous and Heterogeneous Systems	3
1.4	Thermodynamic Equilibrium	4
1.5	State of the System & Processes.....	4
1.6	Pure Substances.....	5
1.7	Zeroth Law of Thermodynamics	7
	<i>Objective Brain Teasers</i>	12
	<i>Conventional Brain Teasers</i>	14

CHAPTER 2

Energy and its Interactions..... 15-45

2.1	Introduction	15
2.2	Work Transfer	16
2.3	Closed System Analysis (Fixed Mass Energy Analysis)	18
2.4	Ideal Gas.....	29
2.5	Heat Transfer	33
2.6	Points to Remember Regarding Heat Transfer and Work Transfer.....	37
	<i>Objective Brain Teasers</i>	38
	<i>Conventional Brain Teasers</i>	42

CHAPTER 3

First Law of Thermodynamics 46-78

3.1	Introduction	46
3.2	The First Law of Thermodynamics (Joule's Law or Law of Conservation of Energy)	46

3.3	Enthalpy (H)	52
3.4	Heat Transfer in Various Processes.....	53
3.5	Free Expansion	68
	<i>Objective Brain Teasers</i>	71
	<i>Conventional Brain Teasers</i>	77

CHAPTER 4

Open System Analysis by First Law 79-120

4.1	Introduction	79
4.2	An Open System (or Control Volume)	79
4.3	Steady Flow Systems	80
4.4	Mass Balance and Energy Balance for Steady Flow Systems	80
4.5	SFEE Applied to Various Devices.....	87
4.6	Comparison of SFEE with Euler and Bernoulli Equations.....	97
4.7	Unsteady Flow Process.....	98
	<i>Objective Brain Teasers</i>	110
	<i>Conventional Brain Teasers</i>	116

CHAPTER 5

Second Law of Thermodynamics 121-167

5.1	Introduction	121
5.2	Thermal Energy Reservoir	122
5.3	Heat Engine	123
5.4	Statements of Second Law of Thermodynamics.....	126
5.5	Refrigerators and Heat Pumps.....	128
5.6	Equivalence of Kelvin-Planck & Clausius Statement ..	132
5.7	Reversible and Irreversible Processes	133
5.8	The Carnot Cycle.....	139

5.9	The Carnot Principles	141
5.10	Thermodynamic Temperature Scale.....	144
5.11	Measures of Maximum Performance for Cycles	
	Operating between Two Reservoirs.....	146
	<i>Objective Brain Teasers</i>	159
	<i>Conventional Brain Teasers</i>	163

CHAPTER 6

Entropy 168-231

6.1	Introduction	168
6.2	Clausius Inequality	168
6.3	The Thermodynamic Property : Entropy	170
6.4	Principle of Increase of entropy	172
6.5	Temperature-Entropy Diagram	175
6.6	The T-dS Relations	178
6.7	Entropy change for an Ideal Gas	180
6.8	Approximate Analysis of entropy change	182
6.9	Entropy Change of An Incompressible Substance...	188
6.10	Finite Body Analysis.....	190
6.11	Reversible Steady-Flow Work.....	197
6.12	Second Law Analysis of a Control Volume.....	199
6.13	Available Energy	202
6.14	Available Energy as Referred to a Cycle.....	203
6.15	Heat Transfer Through a Finite Temperature	
	Difference	204
6.16	Availability and Availability function.....	207
6.17	Irreversibility.....	210
6.18	Second Law Efficiency	211
	<i>Objective Brain Teasers</i>	217
	<i>Conventional Brain Teasers</i>	224

CHAPTER 7

Properties of Pure Substances..... 232-260

7.1	Introduction	232
7.2	Phase Change of a Pure Substance.....	232
7.3	Property Diagrams For phase-change processes	235
7.4	Quality or Dryness Fraction	240
7.5	Enthalpy and Entropy of Pure Substances	243
7.6	Steam Tables.....	245
7.7	Reference State and Reference Values.....	250
	<i>Objective Brain Teasers</i>	252
	<i>Conventional Brain Teasers</i>	255

CHAPTER 8

Thermodynamic Relations..... 261-296

8.1	Introduction	261
8.2	Mathematical Theorems	261
8.3	The Maxwell Relations	263
8.4	Tds Partial Differential Equations	264
8.5	Specific Heats.....	265
8.6	Energy Equations.....	271
8.7	The Joule-Thomson Coefficient	276
8.8	Clausius-Clapeyron Equation	279
8.9	Compressibility Factor	282
8.10	Van der Waal's equation of State.....	284
8.11	Mixture of Ideal Gases.....	285
	<i>Objective Brain Teasers</i>	287
	<i>Conventional Brain Teasers</i>	291



Basic Concepts & Zeroth Law of Thermodynamics

1.1 INTRODUCTION

The name thermodynamics stems from the Greek words **therme (heat)** and **dynamics (power)** which is most descriptive of the early efforts to convert heat into power.

Thermodynamics is the branch of science which deals with the energy and its interactions. More specifically it deals with **energy conversions, energy exchange** and the **direction of exchange**.

Basically it is the science of energy transfer and its effect on the physical properties of substances. It is based upon observations of common experience which have been formulated into thermodynamics laws. These laws govern the principles of energy conversion.

1.1.1 Macroscopic and Microscopic Approach

- **Macroscopic Approach:** In this approach, individual molecular behaviour of the working medium is not taken into consideration and the average behaviour of all the molecules is studied. This approach is applied when the **continuum concept** is valid. For example: Macroscopic quantity, **pressure** is the average rate of change of momentum due to all the molecular collisions on a unit area.
- **Microscopic Approach:** In this approach, the individual molecular behaviour is taken into consideration. For example: It is used in space exploration. From the microscopic point of view, matter is composed of myriads of molecules.

Concept of Continuum : Matter is made up of atoms that are widely spaced in the gaseous phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a **continuous, homogeneous matter with no holes** that is a continuum. The continuum idealization allows us to treat properties as point functions and to assume the properties vary continually in space with no jump discontinuities. Continuum concept can be applied if the **mean free path** is much less than system dimensions. At very high vacuum at or very large elevations, the mean free path may become large. For such cases, the **rarefied gas flow theory** should be used and the impact of individual molecules should be considered.

Mean Free Path : It is the average distance travelled by a molecule between two successive collisions.



For our use, in classical thermodynamics, we often use macroscopic approach. All the results of classical or macroscopic thermodynamics can, however, be derived from the microscopic and statistical study of matter.

1.2 SYSTEM, SURROUNDINGS AND BOUNDARY

1.2.1 System, Surroundings and Boundary

- **System :** A thermodynamic system is defined as the quantity of matter or a region in space (also called **control volume**) upon which our study or analysis is concentrated.
- **Surroundings :** Everything external to the system is called surroundings. The part of the surrounding which is directly affected by the system is called **immediate surrounding**.
- **Boundary :** The real or imaginary surface that separates the system from its surroundings is called boundary. The boundary of a system can be **fixed or movable**. The boundary is the contact surface shared by both the system and the surroundings. Mathematically speaking, the boundary has zero thickness and thus it can neither contain any mass nor occupy any volume in space.

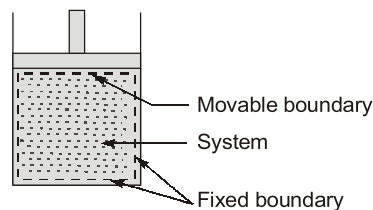


Fig : Fixed Mass System

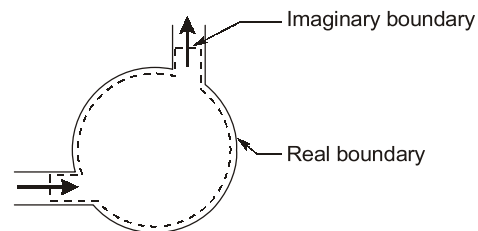


Fig : Fixed Region in Space (Control Volume)

1.2.2 Types of System

Based on energy-mass interaction with the surroundings, thermodynamic systems have been categorized as given below.

Type of system	Energy transfer	Mass transfer	Example
Open	Yes	Yes	Piston cylinder arrangement with valves, compressor, turbine, etc.
Closed	Yes	No	Piston cylinder arrangement without valves
Isolated	No	No	Universe, perfectly insulated closed thermos flask



Control volume is a volume surrounding an open system on which study is focused. The boundaries of a control volume is called control surface.



- In case of an insulated system, mass and work transfer may take place but heat transfer is not possible. For example, an insulated turbine as shown in figure.
- Energy and mass transfer are associated with system and boundaries. Any interactions taking place within the system are not considered while classifying the system.

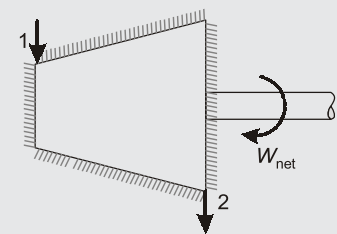


Fig : Insulated Turbine

1.2.3 Properties of a System

- Any characteristic of the system is called as the property of the system.
- Properties are **macroscopic characteristics** of a system such as mass, volume, energy, pressure and temperature to which numerical values can be assigned at a given time **without** knowledge of the past history of the system. They have been classified as follows:

1. Intensive (Intrinsic) Properties: The properties which are **independent** of the mass of system under consideration are known as intensive properties.

Examples: Pressure, temperature, thermal conductivity, viscosity, etc.



REMEMBER

- All specific properties are intensive properties, eg. specific volume, specific heat, specific internal energy, specific entropy, etc.
- Density is an intensive property.

2. Extensive (Extrinsic) Properties: The properties which are **dependent** on the mass of system under consideration are known as extensive properties.

Examples: Mass, energy, volume, entropy, enthalpy, kinetic energy, etc.

NOTE : While deciding whether a property is intensive or extensive we should not change the system under consideration.

- An easy way to determine whether a property is intensive or extensive is to assume that system is divided into two equal parts with an imaginary partition as shown in figure. Each part will have same value of the property in case it is intensive but half the value in case it is extensive.

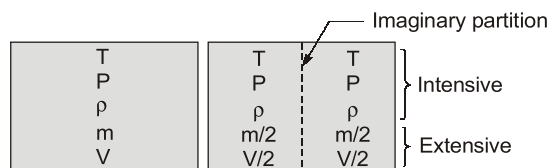


Fig : Intensive and extensive properties

- Important points with respect to properties:**

- They are point or state functions.
- They are independent of past history.

3. They are exact differentials, if E is a property then $\int_1^2 dE = E_2 - E_1$

Example 1.1

Which of the following is an extensive property?

- (a) Refractive index (b) Density
(c) Boiling point (d) Number of moles

Solution : (d)

Number of moles is an extensive property. As we divide the system into parts the number of moles in each part will differ. Thus, it is an extensive property.

1.3 HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

A system consisting of a single phase is called a homogeneous system, while a system consisting of more than one phase is known as a heterogeneous system. A quantity of matter homogeneous throughout in chemical composition and physical structure is called a **phase**.

1.4 THERMODYNAMIC EQUILIBRIUM

A system is said to be in thermodynamic equilibrium if it satisfies following equilibrium conditions:

1. **Thermal equilibrium** : If the **temperature** is same throughout the entire system then the system is said to be thermal equilibrium.
2. **Mechanical equilibrium** : A system is said to be in mechanical equilibrium if there is **no change in pressure** at any point of the system with time.
3. **Chemical equilibrium** : A system is said to be in chemical equilibrium if its **chemical composition** does not change with time that is no chemical reactions occur.
4. **Phase equilibrium** : A system is said to be in phase equilibrium if **mass of each phase** remains constant with time.

1.5 STATE OF THE SYSTEM & PROCESSES

- Any equilibrium condition of the system is called the **state** of the system. At a given state, all the properties of a system have **fixed values** throughout the entire system [may/may not be uniform]
- Any change that a system undergoes from one equilibrium state to another is called a **process**.
- The series of states through which a system passes during a process is called the **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.

A process can be classified as:

1. **Quasistatic and Non-Quasistatic Process**: If a process takes place **infinitely slowly** it is called a quasistatic process, otherwise a non-quasistatic process.

A quasistatic process is generally represented by a solid line on property diagrams. Whereas, a non-quasistatic process is represented by dotted lines as shown in the figure. During a quasistatic process the properties remain **uniform** i.e., every point on the path represents an equilibrium state and hence can be represented on the curve.

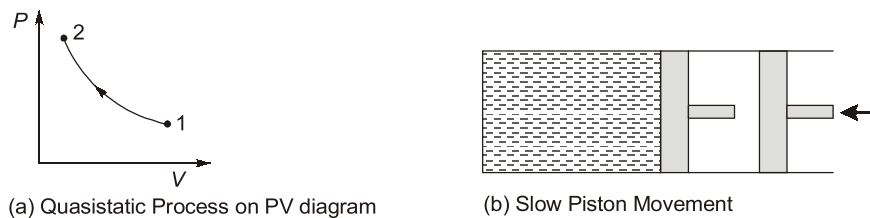


Fig : Slow compression (quasistatic)

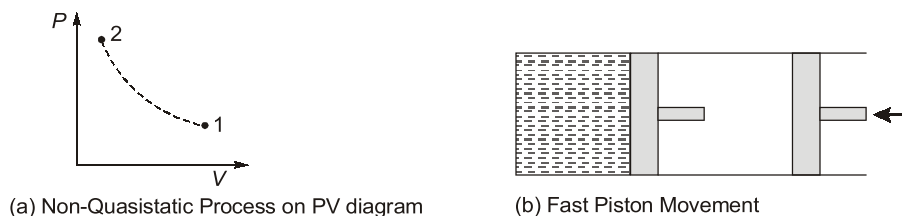


Fig : Very fast compression (non-quasistatic)

- 2. Reversible and Irreversible Process:** A process is said to be reversible if it can be reversed in direction following the same path as that of the forward process without leaving any change in the system as well as the surroundings. Otherwise, it is said to be irreversible.



- Quasistatic and reversible processes are not always same but for our study we take them as same.
- All reversible processes are quasistatic but all quasistatic processes might not be reversible.
- Frictionless quasistatic process is reversible.
- The reversibility of a process in problems can be conveyed in following ways:
 - (a) Quasistatic compression/expansion
 - (b) Ideal flow (open system)

1.6 PURE SUBSTANCES

- A substance is said to be a pure substance if it is of homogeneous and invariable chemical composition throughout its mass.
- It does not have to be a single chemical element or compound. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous. For example: air, steam-water mixture.
- The relative proportions of the chemical elements constituting the substance are also constant in a pure substance.

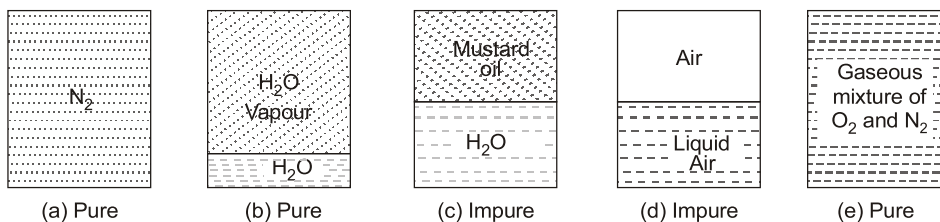


Fig : Examples of Pure and Impure Substances



REMEMBER

- The mixture of refrigerants which behaves as a pure substance is called Azeotrope.
- Mixture of ethyl alcohol and water is also a pure substance due to molecular level hydroxyl bond formation.
- Flue gases, which are the products of combustion of air and fuel, are also considered as a pure substance.
- The mixture of air and liquid air is not a pure substance, since the relative proportions of oxygen and nitrogen differ in gas and liquid phases.

1.6.1 Gibbs Phase Rule

- Phase is defined as a quantity of mass that is homogeneous throughout in chemical composition and physical structure. Eg. solid, liquid, vapour, gas.

- In general the minimum number of independent intensive variables required to fix the state of the system for multiphase, multi-component system is given by the Gibbs phase rule, expressed as:

$$F = C - P + 2$$

where, F = Degree of freedom or minimum number of independent intensive variables (properties) required;
 C = Number of chemical components in the system; P = Number of phases present in equilibrium in the system.



- Gibb's phase rule doesn't include compositional variables.
- The total variables required to fix the state in the wet region is 2.
- The degree of freedom and total variables required to fix the state for saturated liquid and saturated vapour is 1.

Example 1.2

Which of the following systems have more than one degree of freedom?

- (a) Water and water vapour system (b) A mixture of oxygen and nitrogen gas as system
 (c) Water at its triple point (d) None of these

[MSQ]

Solution :(b)

(a)

In the given system it can be asserted that:

Number of phases, $P = 2$ (liquid + vapour)

Number of components, $C = 1$ (only water)

∴ From Gibbs phase rule, we know

$$F = C - P + 2$$

Substituting the values in above equation

$$F = 1 - 2 + 2 = 1$$

Comment : Only one variable is enough to fix the state of the system, for example, two phase systems in evaporators of a refrigeration system.

(b) It can be asserted that in the given system

$P = 1$ (only gas)

$C = 2$ (O_2 and N_2)

From the Gibbs phase rule, we know $F = C - P + 2$

Substituting the values in above equation

$$\begin{aligned} F &= 2 - 1 + 2 \\ &= 3 \end{aligned}$$

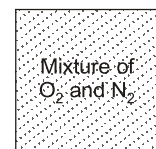
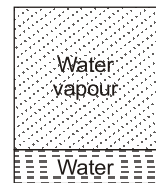
Comment : We will require three independent intensive variables to fix the state of the system.

(c) **Triple point** of any substance is a state at which it can exist in equilibrium in solid, liquid and gaseous phase i.e. all 3 phases can co-exist.

∴ It can be asserted from above definition that at triple point of water

$P = 3$ (solid, liquid and gas)

$C = 1$ (only H_2O)



From the Gibbs phase rule, we know $F = C - P + 2$

Substituting the values in above equation

$$F = 1 - 3 + 2$$

$$= 0$$

Comment : The degree of freedom comes out to be zero which suggests that the triple point of water is a very specific condition and occurs at a particular value of temperature and pressure.

∴ Answer is option (b).



REMEMBER

Triple point of water is defined by following conditions:

$$T = 0.01^\circ\text{C} = 273.16 \text{ K}, \quad P = 0.6112 \text{ kPa}$$

NOTE: Even though air is mixture of several gases, it is considered as one component (in gaseous phase).

1.7 ZEROTH LAW OF THERMODYNAMICS

- It states that if two bodies *A* and *B* are in thermal equilibrium with a third body *C* then *A* and *B* are also in thermal equilibrium with each other.

For example : **Thermometer :** In case of mercury thermometer, the body temperature (*A*) is in thermal equilibrium with thermometer tube (*C*) and thermometer tube (*C*) is in thermal equilibrium with body (*B*) i.e. mercury. So body temperature and mercury are in thermal equilibrium as shown in figure.

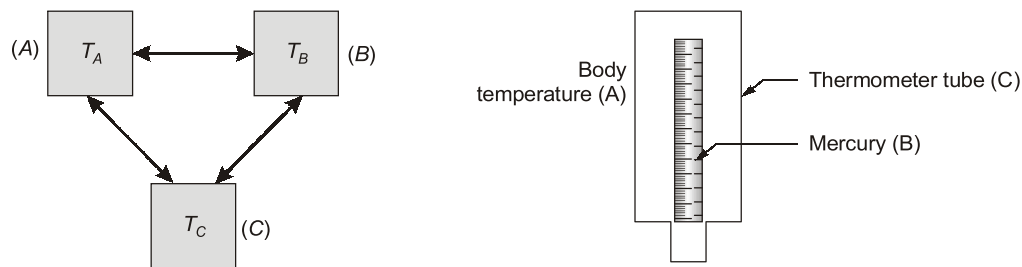


Fig : Zeroth law

Explanation :

Let us say T_A , T_B and T_C are the temperatures of the bodies *A*, *B*, and *C* respectively.

Given: *A* and *C* are in thermal equilibrium i.e., $T_A = T_C$ and *B* and *C* are in thermal equilibrium i.e., $T_B = T_C$ then as a consequence of zeroth law, *A* and *B* will also be in thermal equilibrium i.e., $T_A = T_B$



NOTE

- Zeroth law gives the **concept of temperature and its measurement.**
- Hotness and coldness is a feeling associated with heat transfer rate and temperature is one of the variable which affects the heat transfer.

Do
You
Know ?

Fundamental value of Zeroth law was recognized more than half a century after the formulation of the first and second laws and hence it was named zeroth law as it should have preceded the first and second laws.

Example 1.3

Zeroth law of thermodynamics is not applicable for:

- 20 ml of water 30°C is mixed with 20 ml of H₂SO₄ at 30°C.
- 50 ml of water at 30°C is mixed with 100 ml of water at 30°C.
- 5 kg of wet steam at 100°C is mixed with 50 kg of dry and saturated steam.
- None of the above

Solution : (a)

In case of mixing of water and sulphuric acid, a chemical reaction will take place and an enormous amount of heat is released as mixing is highly exothermic. So, there is no thermal equilibrium any more. Hence, zeroth law is not applicable.

1.7.1 Thermometry

- It is the branch of physics concerned with the measurement of temperature and the design of thermometers.
- It is based on finding the thermometric property.
- The temperature cannot be quantified on the basis of feeling and hence we need a property which is easily measurable and then that property is used to find the temperature of the body.

1. Thermistor or Resistance Thermometer

- It is based on working of a **balanced Wheatstone bridge circuit**.

Here: P and Q = Known resistances

G = Galvanometer which gives direction of flow of current

R = Variable resistance (helps in balancing of Wheatstone bridge)

S = Resistance, very sensitive to temperature change

- Initially let us assume that the circuit is balanced, hence there will be no deflection in the Galvanometer G .
- By balanced Wheatstone bridge equation we can write

$$\frac{P}{Q} = \frac{R}{S} \quad \dots(i)$$

$$S = S_0(1 + At + Bt^2)$$

where, S_0 is the resistance of the platinum wire when it is surrounded by melting ice and A and B are constants.

- Now if we change the temperature of S , its resistance will change to S' (unknown value) and the bridge will become unbalanced.
- Thus we will change value of R (variable resistance) to R' , to again balance the bridge.

Now

$$\frac{P}{Q} = \frac{R'}{S'} \quad \dots(ii)$$

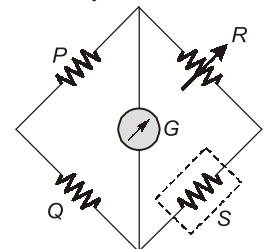


Fig : Wheatstone bridge

- From equation (ii), we get the value of unknown S' at the new temperature.
- The resistance as a function of temperature for resistor S will be known to us and from that we can calculate the temperature.

Remember : In thermistor, **resistance** is the thermometric property used to calculate temperature.

2. Thermocouple

- It's working is based on the principle of **Seebeck effect**.
- Seebeck effect: If two different metals are joined at two different junctions which are kept at different temperatures then an EMF is generated between the two junctions which is directly proportional to the temperature difference between them.

According to Seebeck effect:

$$\text{EMF} \propto (T_2 - T_1)$$

- If one of the temperatures is known, the other can be found easily using the above relation.

Remember : In thermocouple, **EMF** is the thermometric property.

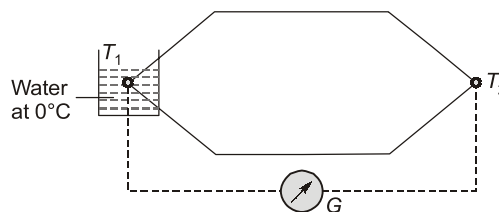


Fig : Seebeck Effect

Do you know? The opposite of Seebeck effect is called **Peltier effect** and it is used in thermoelectric refrigeration.

3. Constant Volume Gas Thermometer

- It is based on **Gay-Lussac's law** which states that for a given mass and constant volume of an ideal gas, the pressure is directly proportional to the absolute temperature.

$$P \propto T$$

or,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

- Here temperature is measured by pressure change.

Remember : **Pressure** is the thermometric property in this case. It is used to measure very low temperature.

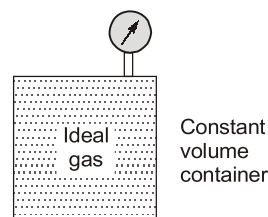


Fig : Constant Volume Gas Thermometer

4. Constant Pressure Gas Thermometer

- It is based on **Charles's law** which states that, for a given mass of an ideal gas at constant pressure, the volume is directly proportional to the absolute temperature.

$$V \propto T$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- Here temperature is measured by volume change.

Remember : **Volume** is the thermometric property in this case.

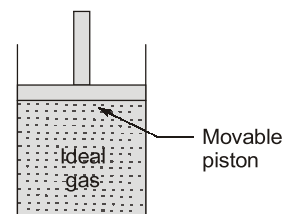


Fig : Constant Pressure Gas Thermometer

$$\Delta t_F = \frac{9}{5} \Delta t_c$$

Putting the value of Δt_c , we get $\Delta t_F = \frac{9}{5} \times 10 = 18^\circ\text{F}$

NOTE: $\Delta t_F = 1.8 (\Delta t_c)$

1.7.3 Calibration of Thermometers

If two different thermometers, using alcohol and mercury respectively, are calibrated at ice point and steam point and the distance between ice point and steam point is divided into 100 equal parts then they are not guaranteed to give the same reading anywhere between the calibration points, but they will always give the same readings at the calibration points itself.

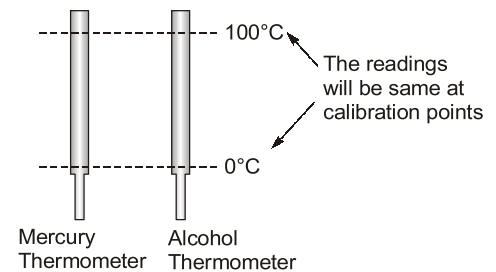


Fig : Calibration of Thermometers

Summary



- Thermodynamics is the science that primarily deals with energy.
- A system with fixed mass is called a closed system and a system that involves mass transfer across its boundary is called an open system.
- Mass dependent properties are called extensive properties and mass independent properties are called intensive properties.
- All temperature measurements are based on Zeroth law.
- Temperature scales are arbitrary or random in nature.



OBJECTIVE BRAIN TEASERS

- Q.1** An open system is the one in which
- Heat and work cross the boundary, but the mass does not
 - Mass crosses the boundary, but the heat and work do not
 - Heat, work and mass cross the boundary
 - None of heat, work and mass cross the boundary
- Q.2** Which of the following is a point function?
- Temperature
 - Pressure
 - Internal Energy
 - Power
- [MSQ]**
- Q.3** Which of the following is an intensive property of a thermodynamic system?
- Volume
 - Temperature
 - Mass
 - Energy
- Q.4** The basis of temperature measurement is
- Zeroth law of thermodynamics
 - First law of thermodynamics
 - Second law of thermodynamics
 - Third law of thermodynamics
- Q.5** The absolute zero pressure will be
- When molecular momentum of the system becomes zero
 - at sea level
 - at a temperature of -273.15 K
 - under vacuum conditions
- Q.6** The standard fixed point for thermometry is the
- ice point
 - triple point of water
 - boiling point of water
 - sulphur point

- Q.7** A system comprising of a single phase is called
 (a) Closed system
 (b) Open system
 (c) Heterogeneous system
 (d) Homogeneous system
- Q.8** A mixture of air and liquid air is
 (a) a pure substance
 (b) not a pure substance
 (c) homogeneous and invariable in chemical composition throughout its mass
 (d) one having relative proportions of oxygen and nitrogen constant in gas and liquid phases
- Q.9** When mean free path of the molecules of a gas approaches the order of magnitude of the dimensions of the vessel, which concept of the following loses its validity?
 (a) Continuum (b) Stability
 (c) Equilibrium (d) Entropy
- Q.10** Most of the real processes are
 (a) quasi-static (b) non-quasi-static
 (c) adiabatic (d) isothermal
- Q.11** The number of independent thermodynamic variables which are required to determine the thermodynamic state of liquid water in equilibrium with saturated steam is
 (a) 0 (b) 1
 (c) 2 (d) 3
- Q.12** Select the correct statement among the following:
 (a) The working principle of thermocouple is Peltier effect.
 (b) Thermocouple consists of two wire legs made from same metal.
 (c) Thermopile is a series connection of thermocouples.
 (d) None of the above is correct
- Q.13** The resistance of the platinum wire at the ice point is 5Ω and at steam point it is 5.39Ω . When the thermometer is inserted in a hot bath, the resistance of the platinum wire is 5.795Ω . The bath temperature is nearly

- (a) 203°C (b) 303°C
 (c) 476°C (d) 0°C

- Q.14** Which of the following is/are the examples of irreversible process?
 (a) Isothermal expansion
 (b) Electrolysis
 (c) Plastic deformation
 (d) Combustion

[MSQ]

ANSWERS KEY

1. (c) 2. (a,b,c) 3. (b) 4. (a) 5. (a)
 6. (b) 7. (d) 8. (b) 9. (a) 10. (b)
 11. (b) 12. (c) 13. (a) 14. (c, d)

HINTS & EXPLANATIONS

11. (b)
 By Gibbs phase rule,

$$F = C - P + 2$$
 ($C = 1 \rightarrow \text{H}_2\text{O}$, $P = 2 \rightarrow \text{Liquid water and steam}$)

$$\Rightarrow F = 1 - 2 + 2$$

$$\Rightarrow F = 1$$
12. (c)
 • Thermocouple works on the principle of Seebeck effect.
 • It consists of two wire legs made from different metals.
 • Thermopile is a series connection of thermocouples.
13. (a)
 The variation of resistance with temperature is given by,

$$\therefore R_T = R_0(1 + \alpha\Delta T)$$

$$\Rightarrow R_{100} = R_0(1 + \alpha\Delta T)$$

$$\Rightarrow 5.39 = 5(1 + \alpha \times 100)$$

$$\Rightarrow \alpha = 7.8 \times 10^{-4}\text{C}^{-1}$$

 Now, $5.795 = 5(1 + (7.8 \times 10^{-4})(T - 0))$

$$\Rightarrow 7.8 \times 10^{-4}T = 0.159$$

$$\Rightarrow T = 203.84^\circ\text{C}$$

14. (c, d)

Examples of nearly reversible processes:

- Isothermal expansion or compression.
- Electrolysis
- Polytropic expansion or compression of fluid.
- Frictionless relative motion.

Examples of irreversible processes:

- Throttling
- Combustion
- Free expansion
- Diffusion
- Plastic deformation
- Electricity flow through a resistor



CONVENTIONAL BRAIN TEASERS

Q.1 The readings of two thermometers A and B agree at ice point and steam point as 0°C and 100°C . The two temperature readings are related by the following expression:

$$t_A = a + bt_B + ct_B^2$$

where a , b and c are constants. In a constant temperature bath, the temperature are shown as 51°C on thermometer A and 50°C on thermometer B . Determine the reading on thermometer B when the thermometer A reads 65°C . Can you comment which of the two thermometers is correct?

1. Solution:

Given: $t_A = a + bt_B + Ct_B^2$

As the reading of two thermometers A and B agree at ice point (0°C) and steam point (100°C).

When $t_A = 0^\circ\text{C}$, t_B is also 0°C

$$0 = a + bt_B + Ct_B^2$$

$$0 = a + b(0) + C(0)^2$$

($a = 0$) $t_A = bt_B + Ct_B^2$

when, $t_A = 100^\circ\text{C}$, t_B is also 100°C

$$100 = b(100) + C(100)^2$$

$$b + (100)C = 1 \quad \dots (i)$$

when, $t_B = 50^\circ\text{C}$, $t_A = 51^\circ\text{C}$

$$t_A = bt_B + Ct_B^2$$

$$51 = (50)b + (50)^2C$$

$$\dots (ii)$$

From equation (i) and (ii)

$$b = 1.04$$

$$C = -4 \times 10^{-4}$$

$$\therefore t_A = 1.04 t_B - 4 \times 10^{-4} t_B^2$$

when, t_A reads 65°C

$$65 = 1.04 t_B - 4 \times 10^{-4} t_B^2$$

or $t_B = 64.07^\circ\text{C}$

None of the two thermometers are ideal. So we cannot comment on to which is more correct.

