UPPSC-AE 2025

Uttar Pradesh
Public Service Commission

Combined State Engineering Services Examination

Assistant Engineer

Mechanical Engineering

Thermodynamics

Well Illustrated **Theory** *with*
Solved Examples and **Practice Questions**

MADE EASY PUBLICATIONS

Thermodynamics

Contents

CHAPTER 1 Introduction

1.1 Introduction

Thermodynamics is the science of energy transfer and its causes and effects.

Thermodynamics can be studied upto two ways:

- In microscopic thermodynamics, the behaviour of the gas is described by summing up the behaviour of each molecule.

  In **macroscopic** thermodynamics, the behaviour of the gas is described by the net effect of action of all the molecules, which can be perceived by human senses.
- A **system** is a matter or region on which analysis is done. System is separated from the surrounding by boundary. Everything external to the system is called ***surroundings***. System & surrounding together is called a *universe*.

	Mass Transfer	Energy Transfer	Example
Open	Yes	Yes	Compressor, Turbine etc.
Close	No	Yes	Piston cylinder arrangement, gas in a closed container.
Isolated	No	No	Universe

Control Mass: Analysis of system based on fixed amount of matter.

Control Volume: Volume surrounding an open system on which study is focused.

1.1.1 Concept of Continuum

- Continuum hypothesis suggests that the matter is continuously distributed with no voids being present.
- In case of gases it is valid when mean free path (average distance travelled by a molecule between two successive collisions is much smaller than the system dimensions.)
- In case of "Rarefied gases theory" the concept of continuum is not valid.

1.2 Properties

- Every system has certain characteristics by which its physical condition may be described. Example:- Volume, temperature, pressure. Such characteristics are called properties of the system.
- These are all macroscopic in nature.
- Properties are point function and are exact or perfect differentials.

  Example: Internal energy, enthalpy, entropy

1.2.1 Categories of Properties

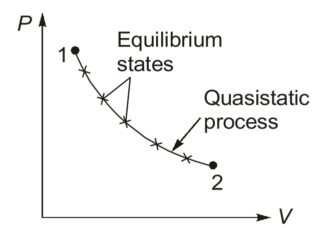
Catagories of Properties

Intensive Properties
Properties are independent of mass.
Ex. pressure, temp. density, specific vol.,
Specific heat (c_p, c_v) etc.

Extensive Properties
Properties are related to the mass.
Ex. volume, energy,
Heat capacity (c_v, c_p)

1.2.2 Specific Extensive Properties

- Extensive properties per unit mass is specific extensive properties.
- It is an intensive property.
  Example:- Specific volume, Specific energy.
- It is independent of mass.



A quasi-static process

1.2.3 State

It gives the complete description of the system.

1.2.4 Phase

It is a quantity of mass that is homogeneous throughout in chemical composition and physical structure. Example:- solid, liquid, vapour, gas.

1.2.5 Path and Process

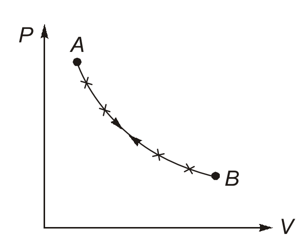
The succession of states passed through during a change of state is called the path of the system. A system is said to go through a process if it goes through a series of changes in state.

1.2.6 Quasistatic Process

Infinite slowness is the characteristic feature of quasistatic process. All states of the system passes through the equilibrium states.

1.3 Reversible Process or Ideal Process

- The process which can be reversed without leaving any effect on system and surrounding is called as reversible process.
- All reversible processes can be shown on diagrams. Example:- P–V, T–S, P–T diagrams.
- A reversible process is carried out infinitely slowly with an infinitesimal gradient. Hence every state passed through by the system is an equilibrium state. So a reversible process coincides with a quasi-static process.
- A quasi-static process without friction is reversible process.
- All reversible processes are quasi-static process but all quasi-static process are not reversible.
- If the time allowed for a process to occur is infinitely large, even through the gradient is finite, the process becomes reversible.



A reversible process

Example - 1.1 A reversible process

(a) Must pass through a continuous series of equilibrium states.
(b) Leaves no history of the events in surroundings.
(c) Must pass through the same states on the reversed path as on the forward path.
(d) All options are correct

Solution: (d)

Example - 1.2 Which of the following is/are reversible process(es)

1. Isentropic expansion
2. Slow heating of water from a hot source.
3. Constant pressure heating of an ideal gas from a constant temperature source.
4. Evaporation of a liquid at constant temperature.

Select the correct answer using the code given below:

(a) 1 only (b) 1 and 2
(c) 2 and 3 (d) 1 and 4

Solution: (b)

1.4 Irreversible Process or Natural Process

- An irreversible process is a process that cannot be retained to their original conditions. That is the system and the surroundings would not return to their original conditions if process was reserved.
- All spontaneous processes are irreversible process.
- Irreversible process cannot be shown on diagrams. They are shown as dotted lines.

  Example:- Heat transfer through finite temperature difference, Free expansion, mixing of fluids, presence of friction.
- A system will be in a state of thermodynamic equilibrium if the conditions for the following three types of equilibrium are satisfied.
  (i) Mechanical equilibrium
  (ii) Chemical equilibrium
  (iii) Thermal equilibrium

1.5 A Pure Substance

- A substance homogeneous in chemical composition and homogeneous in chemical aggregation is called as pure substance.

  Examples of Pure Substance: Atmospheric air, steam water mixture and combustion products of a fuel.
- Mixture of air and liquid air is not a pure substance since the relative proportion of oxygen and nitrogen differ in gas and liquid phases in equilibrium.

NOTE

1. Vapour is the gaseous phase of a substance when it is very close to condensation.
2. Steam is special word given to the gaseous form of water only when generate it is present only at high temperatures.
3. Mixture of refrigerant behaving as pure substance is called azeotrope or azeotropic mixtures.
4. Mixtures of gases is always pure substance at equilibrium.

Example - 1.3 Assertion (A): Water is not a pure substance.

Reason (R) : The term pure substance designates a substance which is homogeneous and has the same chemical composition in all phases.

(a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
(b) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true.

Solution: (d)

Assertion is false, Reason is true. Water for all practical purpose can be considered at pure substance because it is homogeneous and has same chemical composition under all phases.

1.5.1 Gibb's Phase Rule

The phase rule described the possible number of degree of freedom in a closed system at equilibrium, in terms of the number of separate phases and the number of chemical constituents in the system.

It can be expressed as: $P + F = C + 2$

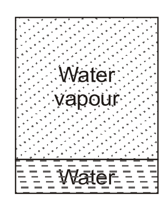
P = Number of phases; F = Degree of freedom; C =Number of component

Example - 1.4 Determine the degree of freedom of the following systems and comment on the result:

(1) Water and water vapour system
(2) A mixture of oxygen and nitrogen gas as system
(3) Water at its triple point

Solution:

(1) In the given system,



$$\text{Number of phases, } P = 2 \quad \text{(liquid + vapour)}$$

$$\text{Number of components, } C = 1 \quad \text{(only water)}$$

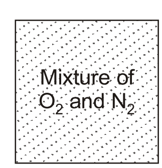
∴ From Gibbs phase rule,

$$P + F = C + 2$$

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

Comment : Only one variable is enough to fix the state of the system.

(2) It the given system,



$$P = 1 \quad \text{(only gas)}$$

$$C = 2 \quad (O_2 + N_2)$$

$$P + F = C + 2$$

$$F = 2 + 2 - 1 = 3$$

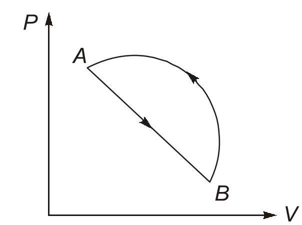
Comment : We will require 3 independent intensive variables to fix the state of the system.

(3)

$$P = 3 \quad \text{(solid, liquid and gas)}$$
$$C = 1 \quad \text{(only water)}$$
$$F = C - P + 2$$
$$F = 1 - 3 + 2 = 0$$

Comment: Triple point of water is a fix point at particular pressure and temperature. $P_{TP} = 0.6112$ kPa $T_{TP} = 0.01°C = 173.16$ k

1.6 Thermodynamic Cycle



- It is a series of processes when initial and final points are same.
- There is no change in property of system.
- Minimum number of processes required for a cycle are 2.

1.7 Temperature

Temperature is a measure of the average kinetic energy of the atoms or molecules.

1.7.1 Zeroth Law of Thermodynamics

- When a body A is in thermal equilibrium with a body B & also separately with a body C then body B & C will be in thermal equilibrium with each other.
- Zeroth law of thermodynamics is the basis of temperature measurement.

1.7.2 Thermometry

- It is based on finding the thermometric property.

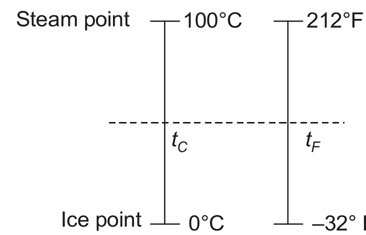
Thermometer	Thermometric property
Constant volume gas thermometer	Pressure (P)
Constant pressure gas thermometer	Volume (V)
Electrical resistance thermometer	Resistance (R)
Thermo couple	EMF (E)
Mercury in glass thermometer	Length (L)

Thermometer	Temperature Range
Platinum resistance Thermometers	–200°C to 1200°C
Thermoelectric thermometers	–200°C to 1600°C
Radiation pyrometers	above 400°C
Segar cone	600°C to 2000°C
Optical pyrometers	above 650°C
Gas thermometers	–200°C to 1200°C

- Thermocouple uses copper-constantan, platinum-rhodium, chromel-alumel combinations.

1.7.2 Temperature Scales

- There are three temperature scales in use today, Fahranheit, celsius and kelvin.
- The interrelationship between Fahreinheit and celsius scale is given below:



$$\frac{t_C - 0}{100 - 0} = \frac{t_F - 32}{212 - 32}$$

$$T_k = t_C + 273.15$$

t_c = Temperature in °C

t_f = Temperature in °F

T_k = Temperature in Kelvin

- Before 1954, temperature measurement was based on two reference point namely ice point and steam point. After 1954, the temperature measurement has been based upon single reference point is triple point of water.
- According to internationally accepted convention.

$$1\text{ K} = \left(\frac{1}{273.16}\right)^{th} \text{ of triple point of water}$$

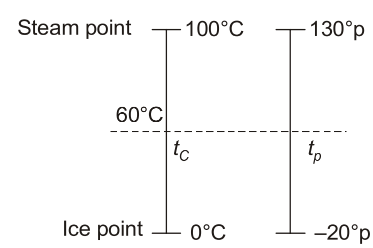
Conversion of temperature unit:

$$\frac{°C}{5} = \frac{°F - 32}{9} = \frac{T - 273.15}{5}$$

°C → Temperature in degree Celsius; °F → Temperature in degree Fahrenheit
T → Temperature in Kelvin

Example - 1.5 The boiling and freezing points of water are marked on a temperature scale *P* as 130°p and –20°p respectively. What will be the reading on this scale corresponding to 60°C on celsius scale?

(a) 60°p (b) 70°p
(c) 90°p (d) 110°p



Solution: (b)

$$\frac{t_c - 0}{100 - 0} = \frac{t_p - (-20)}{130 - (-20)}$$

$$\Rightarrow \quad \frac{60}{100} = \frac{t_p + 20}{150}$$

$$\Rightarrow \quad t_p = 70°p$$

1.8 Ideal Gas Equation

A hypothetical gas which obeys $(p\bar{v} = \bar{R}T)$ at all pressures and temperatures is called an ideal gas

$$p\bar{v} = \bar{R}T \quad \Rightarrow \text{Ideal gas equation}$$

where molar volume, $\bar{v} = \frac{V}{n}$ m^3/kg mol

Absolute pressure, P (in Pa); Absolute temperature, T (in k); n = number of kg moles of the gas

$\bar{R}$ = universal gas constant = 8.3143 kJ/kgmol-K

→ As $p \to 0$ or $T \to \infty$, the real gas approaches the ideal gas behaviour.

$$pV = mRT$$

R = characteristic gas constant

$$= \frac{\bar{R}}{M} \text{ in kJ/kgK} \qquad (\text{Here } M = \text{molecular mass of the gas})$$

1.9 The Gas Laws

All gases generally show similar behaviour when the conditions are normal, but with a slight change in physical conditions like pressure, temperature, or volume these show a deviation. Gas laws are an analysis of this behaviour of gases.

1.9.1 Boyle's law

It states that volume is inversely proportional to pressure when the temperature and the number of molecules are constant.

$$P \propto \frac{1}{V}$$

$$\Rightarrow \qquad P = (k_1) \times \frac{1}{V}$$

where, k_1 = Proportionallly constant ; V = Volume ; P = Absolute value

1.9.2 Charle's Law

Jacques Charles in 1787 analysed the effect of temperature on the volume of gaseous substance at constant pressure.

According to his findings, at constant pressure and for constant mass, the volume of a gas is directly proportional to the temperature.

In his experiment he calculated that the increase in volume with every degree equals $\frac{1}{273.15}$ times of the original volume.

∴ If $T = 0°C$, $V = V_0$, then $T = 7°C$, V_t is given by

$$V_t = V_0 + \frac{t}{273.15} V_0$$

$$\Rightarrow \qquad V_t = V_0\left(1 + \frac{t}{273.15}\right)$$

For the purpose of measuring the observations gaseous substance at temperature 273.15 K, we use a special scale called the "Kelvin Temperature Scale".

The observation of temperature (T) on this scale is 273.15 greater than the temperature (t) of the normal scale.

$$T = 273.15 + t$$

So, according to Charle's law,

$$v \propto T$$

$$\Rightarrow \qquad V = K_2 T$$

Example - 1.6 According to the which law, all perfect gases change in the volume by $\frac{1}{273^{rd}}$ of their original volume at 0°C for every 1°C change in temperature when pressure remains constant?

(a) Joule's law
(b) Boyle's law
(c) Gas-Lussac law
(d) Charle's law

Solution: (d)

1.9.3 Gay Lussac's law

In 1802, a french scientist Joseph Louis Gas-Lussac discovered that at fixed volume and mass of gas, the absolute pressure of that gas is directly proportional to the absolute temperature.

$$P \propto T \qquad T \text{ in (k)}$$

$$\Rightarrow \qquad \frac{P}{T} = k_3 = \text{constant}$$

1.9.4 Avagadro's law

Avagadro's law states that the volume of a *g*-mol of all gases at the pressure of 760 mm of Hg and temperature of 0°C is the same, and is equal to 22.4 litres. Therefore, 1 kg mol of a gas has a volume of 22.4 m^3 at normal temperature and pressure (NTP).

NOTE

at NTP:	T = 0°C = 273.15 k
	P = 760 mm of Hg = 1 atm
at STP:	T = 25°C = 298 k
	P = 1 atm

In other words, this law implies that in unchanged conditions of temperature and pressure. The volume of any gas is directly proportional to the number of molecules of that gas,

$$V \propto n$$

$$\Rightarrow \qquad V = k_4 n$$

Example - 1.7 In case of Boyle's law, if pressure increases by 1% the percentage decreases in volume is

(a) $\frac{1}{101}\%$ (b) $\frac{100}{101}\%$

(c) $\frac{1}{100}\%$ (d) 0%

Solution: (b)

According to Boyle's law, $P_1V_1 = P_2V_2$

$$\Rightarrow \qquad P_1V_1 = 1.01 P_1 V_2$$

$$\Rightarrow \qquad V_1 = 1.01 V_2$$

$$\Rightarrow \qquad V_2 = \frac{1}{1.01} V_1$$

$$\text{Percentage decrease in volume} = \frac{V_1 - V_2}{V_1} \times 100 = \frac{V_1 - \frac{V_1}{1.01}}{V_1} \times 100 = \frac{100}{101}\%$$

1.10 Kinetic Theory of Gases

The kinetic theory of gases attempts to explain the microscopic properties of a gas in terms of the motion of its molecule.

Three Basic Assumptions:

1. The gas consists of identical particles (or atoms/molecules) of mass, m, in constant random (straight line) motion.
2. The size of the molecules are negligible, such that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules interact only through brief, infrequent and elastic collisions.

NOTE : (i) Gas particles move with constant speed between collisions.
(ii) Gravity has no effect on molecular motion.

1.11 Thermodynamics Equilibrium

Thermodynamic equilibrium exists only when all the following types of equilibriums are satisfied :

1. **Thermal Equilibrium :** It is equality of temperature.
2. **Mechanical Equilibrium :** Equality of forces, i.e., pressure at any point should not change with time.
3. **Chemical Equilibrium :** No chemical reaction potential should be present, i.e., no chemical change should place with time.
4. **Phase Equilibrium :** Mass of each phase should not change with time.

Student's Assignment

Q.1 Pressure reaches a value of absolute zero :
(a) at a temperature of –273 K
(b) under vacuum condition
(c) at the earth's centre
(d) when molecular momentum of system becomes zero.

Q.2 Number of components (C), phase (P) and degree of freedom (F) are related by Gibbs phase rule as :
(a) $C - P = F + 2$ (b) $F - C = P + 2$
(c) $C + F = P + 2$ (d) $F + P = C + 2$

Q.3 Molar specific heats of an ideal gas depends on :
(a) Its pressure
(b) Its temperature
(c) Both its pressure and temperature
(d) The number of atoms in a molecule

Q.4 The correct sequence of the decreasing order of the value of characteristic gas constants of the given gases is
(a) hydrogen, nitrogen, air, carbon dioxide
(b) carbon dioxide, hydrogen, nitrogen, air
(c) air, nitrogen, carbon dioxide, hydrogen
(d) nitrogen, air, hydrogen, carbon dioxide

Q.5 Which one of the following thermodynamic processes approximates the steaming of food in a pressure cooker?
(a) Isenthalpic
(b) Isobaric
(c) Isochoric
(d) Isothermal

Q.6 Hot coffee stored in a well insulated thermos flask is an example of
(a) isolated system
(b) closed system
(c) open system
(d) non-flow adiabatic system

Q.7 In highly rarefied gases, the concept of this loses validity
(a) Thermodynamic equilibrium
(b) Continuum
(c) Stability
(d) Macroscopic viewpoint

Q.8 A control volume is
(a) an isolated system
(b) a closed system but heat and work can cross the boundary
(c) a specific amount of mass in space
(d) a fixed region in space where mass, heat and work can cross the boundary of that region.

Q.9 Which one of the following represents open thermodynamic system?
(a) Manual ice cream freezer
(b) Centrifugal pump
(c) Pressure cooker
(d) Bomb calorimeter

Q.10 Which one of the following is the extensive property of the system?
(a) Volume (b) Pressure
(c) Temperature (d) Density

Q.11 Water vapour can be considered as Ideal Gas.
(a) Never
(b) Always
(c) At high pressure
(d) At low pressure

Q.12 Pressure exerted by a gas in a closed container is :
(a) Weak function of Density and Temperature
(b) Weak function of Density and Volume
(c) Strong function of Density and Temperature
(d) Strong function of Density and Volume

Q.13 The sequence of processes that eventually returns the working substance to its original state is known as
(a) Event
(b) Process
(c) Thermodynamic property
(d) Thermodynamic cycle

Q.14 Which conversion is correct?
(a) 1 kWh = 3.6×10^6 Nm
(b) 1 Nm = 0.238×10^{-3} kcal
(c) 1 HP hr = 0.746 kWh
(d) 1 kcal = 4.1868 Nm

Q.15 Heat and work are :
(a) Intensive properties
(b) Extensive properties
(c) Point functions
(d) Path functions

Q.16 According to kinetic theory of gases, at absolute zero _______
(a) specific heat of molecules reduces to zero.
(b) kinetic energy of molecules reduces to zero.
(c) volume of gas reduces to zero.
(d) pressure of gas reduces to zero.

Q.17 Total heat of a substance is also known as
(a) Internal energy (b) Entropy
(c) Thermal capacity (d) Enthalpy

Q.18 Gases have
(a) two specific heats
(b) three specific heats
(c) one specific heats
(d) none of these

Q.19 Universal gas constant of a gas is the product of molecular weight of the gas and
(a) gas constant
(b) specific heat at constant pressure
(c) specific heat at constant volume
(d) none of these

Q.20 Which thermometer is independent of the substance or material used in its construction?
(a) Memory thermometer
(b) Alcohol thermometer
(c) Ideal gas thermometer
(d) Resistance thermometer

Q.21 The definition of 1 K as per the internationally accepted temperature scale is
(a) 1/100th the difference between normal boiling point and normal freezing point of water
(b) 1/273.15th the normal freezing point of water
(c) 100 times the difference between the triple point of water and the normal freezing point of water
(d) 1/273.16th of the triple point of water

Q.22 The pressure P of a gas in terms of its mean kinetic energy per unit volume E is equal to

(a) $E/3$ (b) $E/2$
(c) $3E/4$ (d) $2E/3$

Q.23 A process in which heat is supplied or rejected from the system and entropy is not constant is known as

(a) isothermal (b) isentropic
(c) polytropic (d) hyperbolic

Q.24 In highly rarefied gases, the concept of this loses validity :

(a) Thermodynamic equilibrium
(b) Continuum
(c) Stability
(d) Macroscopic view point

Q.25 Which one of the following substances has constant specific heat at all pressures and temperatures?

(a) Mono-atomic gas
(b) Di-atomic gas
(c) Tri-atomic gas
(d) Poly-atomic gas

Q.26 Measurement of temperature is based on which law of thermodynamics?

(a) Zeroth law (b) First law
(c) Second law (d) Third law

ANSWER KEY — STUDENT'S ASSIGNMENT

1. (d)	**2.** (d)	**3.** (d)	**4.** (a)	**5.** (c)
6. (a)	**7.** (b)	**8.** (d)	**9.** (b)	**10.** (a)
11. (d)	**12.** (c)	**13.** (d)	**14.** (d)	**15.** (d)
16. (b)	**17.** (d)	**18.** (a)	**19.** (a)	**20.** (c)
21. (d)	**22.** (d)	**23.** (c)	**24.** (b)	**25.** (a)
26. (a)				

HINTS & SOLUTIONS — STUDENT'S ASSIGNMENT

1. (d)

According to kinetic theory of gases, the molecules of gases are in continuous random motion and during this random motion, they collide with another one at whatever comes their way. Hence, the average normal force per unit area due to these collision's is pressure. The pressure in the gases is a function of density (number of molecules colliding per unit area).
Therefore, if the collisions of molecules is zero, then the pressure reaches at absolute zero.

2. (d)

According to Gibbs phase rule :

$$P + F = C + 2$$

where, C = No. of components; F = Degree of freedom; P = No. of phases (liquid, solid, gas)

3. (d)

Molar specific heats of an ideal gas depends on the number of atoms in a molecule.

4. (a)

Characteristic gas constant,

$$R = \frac{\text{Universal gas constant}}{\text{Molecular weight}}$$

Hence, $R \propto \dfrac{1}{\text{Molecular weight}}$

Molecular weight of gases are
Hydrogen : 2
Nitrogen : 28
Air : 29
Carbon dioxide : 44

Hence $R_{H_2} > R_{N_2} > R_{Air} > R_{CO_2}$

5. (c)

Volume of pressure cooker is always constant, hence it is isochoric process.

6. (a)

Hot coffee stored in a well insulated thermo-flask is an example of isolated system in which neither mass nor energy transfer takes place.

7. (b)

In highly rarefied gases, since the density is very less matter cannot be assumed to be continuously distributed throughout the space. Hence the concept of continuum loses its validity.