CHEMICAL ENGINEERING

REVISED AS PER NEW GATE Syllabus

STUDY MATERIAL

THERMODYNAMICS

"GATE does not test how much you have studied.
It tests how well you have understood the core concepts
and how fast you can apply them."

Thermodynamics: Marking Analysis in GATE

Year	1 Mark	2 Marks	Total Marks
2026	1 × 3	2×3	9
2025	1 × 2	2×5	12
2024	1 × 1	2×3	7
2023	1 ×3	2×3	9
2022	1 ×4	2×3	10
2021	1 ×2	2×4	10
2020	1 ×2	2×6	14
2019	1 × 4	2 × 4	12
2018	1 × 3	2 ×5	13
2017	1 × 3	2 ×4	11
2016	1 × 3	2 × 3	9
2015	1 × 4	2 ×4	12
2014	1 × 4	2 ×3	10
2013	1 × 2	2 ×5	12
2012	1 × 2	2 × 4	10
2011	1 × 2	2 × 3	8
2010	1 × 1	2 ×4	9

Smart Preparation Strategy for GATE Chemical Engineering

Success in GATE is not about studying everything — it's about studying **the right things, in the right order, with the right intensity**.

Focus on **High Weightage Subjects** first, build strong fundamentals, and then move to advanced problem-solving. This smart approach will not only save your time but also give you **unmatched confidence** on exam day.

GATE SYLLABUS : THERMODYNAMICS

First and Second laws of thermodynamics. Applications of first law to close and open systems. Second law and Entropy. Thermodynamic properties of pure substances: Equation of State and residual properties, properties of mixtures: partial molar properties, fugacity, excess properties and activity coefficients; phase equilibria: predicting VLE of systems; chemical reaction equilibrium

Year	Approx. Questions	Approx. Marks	Major Topics Asked	Difficulty
GATE 2024	6–7 Questions	10–11 Marks	First Law, Entropy, EOS, Fugacity, VLE, Reaction Equilibrium	Moderate
GATE 2025	5–6 Questions	9–10 Marks	Residual Properties, Open System, Activity Coefficient, VLE, Gibbs Free Energy	Moderate–Tough
GATE 2026	6 Questions	9 Marks	Kirchhoff's Law (Emissivity = Absorptivity), Polytropic Process (n for isobaric), Heat of Reaction , Phase Equilibrium, Fugacity, Partial Molar Properties	Moderate

Expected Weightage for GATE 2027

Topic	Expected Weightage
VLE & Fugacity	3–4 Marks
Entropy & Second Law	2–3 Marks
EOS & Residual Properties	2–3 Marks
Reaction Equilibrium	1–2 Marks
Partial Molar Properties	1–2 Marks

Recommended Resources
✓ Fogler (5th Edition)
✓ Levenspiel
✓ GATE SOLVED PAPERS (2000–2026) By Engineers-Institute
✓ Lecture Notes (Online/Offline Classes), Online Mock Test Series By Engineers-Institute
✓ Recorded Video Lectures

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Chapter-1

INTRODUCTION

The word "Thermodynamics" originates from Therme (means heat) + dynamic (means force). The subject is concerned with the interrelation between energy and change of state of any real world system.Thermodynamics forms the basis for the study of a vast variety of devices such as refrigerators, air conditioners, aircraft, power plant etc, the application of which is involved in the everyday life of almost every individual.Every thermodynamics equipment / device makes use of a working substance on which the processes are executed.Most commonly utilized working substances are water and air.H_2O is the working substance in steam power plant; air is the working substance in petrol and diesel engines, etc.The subject of thermal sciences deals with relations between the relevant properties of working substances, energy interactions and inter conversions in the form of 'work' and 'heat'.It is the science of relations between heat, work and the properties of the system.

Thermodynamic system: It is defined as a quantity of matter or region in space chosen for study.For the purpose of thermodynamic analysis, it is necessary to define a 'system'

Surrounding: The mass or region outside the system is said to be the surrounding. For all practical purposes, in any thermodynamic analysis of a system it is necessary to include only the immediate surroundings in which the effects are felt.

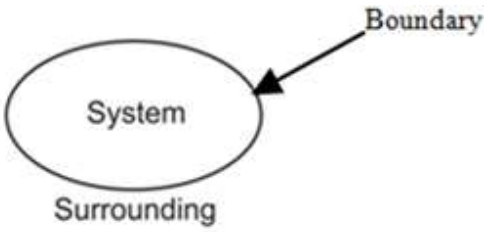

Fig.1.1. Thermodynamic system

Boundary: The real or imaginary surface that separates the system forms its surroundings. It may change in shape as well as in size over time, i.e., increase or decrease

Universe: A system and its surrounding together comprise a universe

Q. 1 How does one characterize the changes that occur in the system during any thermodynamic process?Ans.This can be done if one could measure the change in terms of some properties of the system.

A thermodynamic system is, thus, characterized by its properties, which are the descriptors of state of system.

1.1. Some important concepts about system:

Properties of system

The descriptive characteristic of a system are called its properties such as pressure P, temperature T, volume V, mass m and moles n.Properties are supposed to be either intensive or extensive.Intensive properties are those that are independent of the mass or numbers of moles of the system e.g. temperature, pressure and density.Extensive properties are those whose value depends on the size of the system (mass or moles) e.g. total mass, total volume, etc.The ratio of two extensive properties of a homogeneous system is called intensive property. e.g. specific volume. If an extensive property is divided by the mass or number of moles of a substance forming a system, then intensive property is called a specific property or molar property respectively e.g. specific volume, molar volume, etc.

Molar properties are denoted by $\overline{V}$, $\overline{H}$, etc.

Specific properties are denoted by v, h, etc.

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

Specific gravity is defined as the ratio of density of the substance to that of standard or reference substance (air is taken as reference substance of gases and water for liquid).

Mass density (also known as simple density) is the ratio of change of mass with volume, also known as specific density. It is the reciprocal of specific volume.

Molar density is defined in a similar manner and is reciprocal of molar volume.

Classes of system

(a) Closed system

(b) Open system

(c) Isolated system

Closed system: It is a system of fixed mass. There is energy transfer (i.e. heat or work can cross the system boundary) but no mass transfer can occur across the system boundary. e.g. A certain quantity of fluid in a cylinder bounded by a piston.

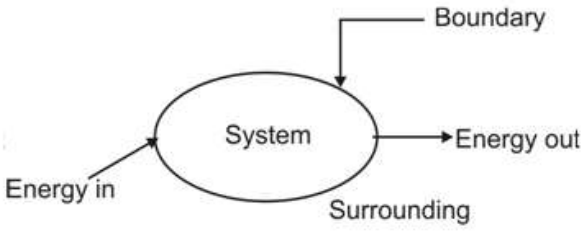

Fig.1.2. Closed system

Open system: A system in which mass and energy crosses the boundary of the system. e.g. An air compressor in which air enters at low pressure and leaves at high pressure

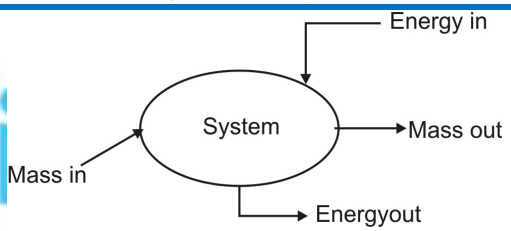

Fig.1.3. Open system

Isolated system: It is one in which there is no interactions between the system and the surroundings.Hence neither mass transfer nor energy transfer take place across the system boundary.

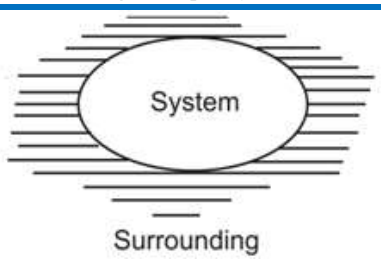

Fig.1.4. Isolated system

Homogeneous and Heterogeneous system:

Phase: A quantity of matter homogeneous throughout in chemical composition and physical structure is said to be phase. viz, solid, liquid and gas

Homogeneous system: A system including of single phase is called homogenous system.

Heterogeneous system: A system consisting of more than one phases is said to be a heterogeneous system.

1.2. Thermodynamic Properties, processes and cycles:

Thermodynamic Equillibrium: A system is known to exist in a state of thermodynamic Equillibrium when no change in any macroscopic property is registered, when the system is isolated from its surroundings. Change of state of a thermodynamic system results from existence of gradients of various types within or across its boundary. Temperature gradient results in heat transfer, velocity gradient results in momentum transfer, concentration gradient results in mass transfer. As long as these gradients exist, system will undergo a change of state. The result of all such changes is to nullify the gradients. The ultimate limit where all gradients are non – existent and system undergoes no further changes is the **'state of thermodynamic Equillibrium'**.For a system in thermodynamic Equillibrium, it needs to also satisfy the criteria for mechanical, chemical and thermal Equillibrium.

State: When all the properties (pressure, volume, temperature) of a system have definite values, the system is known to be at a definite state. Fig. 1.5.shows two different states of a thermodynamic system.

Path: The succession of states passed through at the time of a change of state is said to be the path of the change of state.

Process: When the path is fully specified, the change of state is known as process. e.g. constant pressure process, constant volume process or any change that a system undergoes from one Equillibrium state to another is called a process

Cycle: As a series of state changes such that the final state is identical with initial state. As shown in fig.1.6. "a-b" is a process and "1-2-1" is a cycle.

Thus in a cyclic process, initials states coincides with the final state.

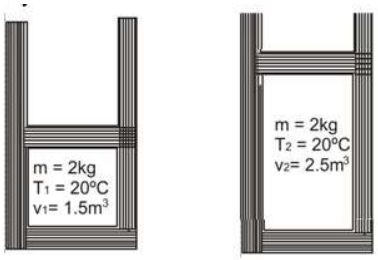

fig: (a) State 1 fig: (b) State 2

Fig. 1.5. Diagrammatic representation of two states of a system

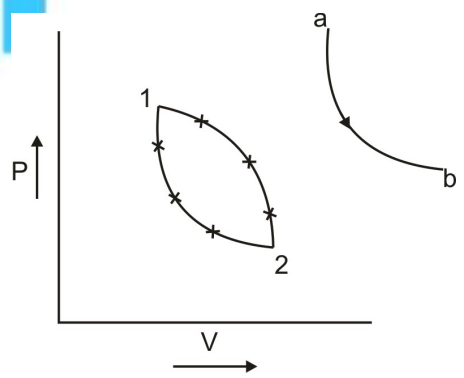

Fig.1.6. Pictorial represenation of a cyclic process

Mechanical Equillibrium: Absence of any unbalanced force within the system itself and between the surroundings and the system.

Chemical Equillibrium: If its chemical composition does not change with time, i.e. no chemical reaction happen.

Thermal Equillibrium: When there is no spontaneous change in any property of the system.

Quasi–static process: A quasi–static process is one which occurs in such a way that changes in one part does not occur faster than other part of the system. Hence, the deviation from thermodynamic Equillibrium is very small. All states of the system passes through are Equillibrium states. In the system (as shown in fig.1.7.), if the weights are removed slowly, one at a time, and the system is allowed to come to Equillibrium after every removal of weight, thesystem could be supposed as undergoing a quasi-Equillibrium or quasi–static process.If, whereas, all the weights are removed suddenly, the piston will jump up and strike the stoppers.Therefore quasi – static process is supposed to take place very slowly in each step.

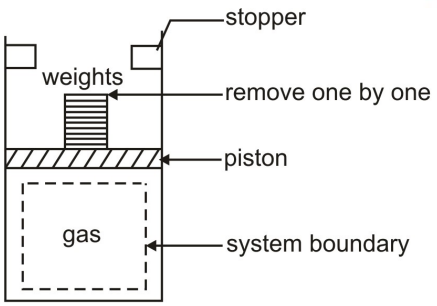

Fig.1.7. Carrying out a Quasi-Equillibrium process on a gas by removal of weights in infinitesimal steps

1.3. Zeroth Law of Thermodynamics:

Zeroth law of thermodynamics is the most basic law applicable for all thermodynamics system. Since first law of thermodynamics was commenced earlier than this law, it was named zeroth law of thermodynamics, instead of first law (as used in usual convention). It states that when a body X is in thermal Equillibrium with a body Y, and also separately in thermal Equillibrium with a body Z, then Y and Z will be in thermal Equillibrium with each other. The Zeroth law also provides the basis for the measurement of temperature.

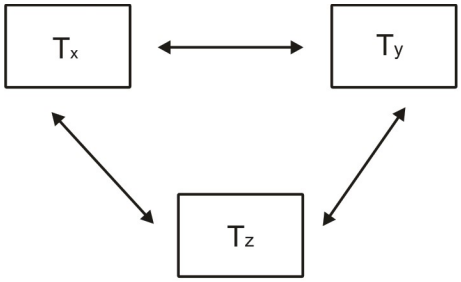

Fig. 1.8. Zeroth law of thermodynamics

Classical Thermodynamics: The study of thermodynamics that does not require knowledge of the behavior of individual particle. This is the thermodynamic studied by the engineers. The laws of classical mechanics are applicable in this case.

Statistical Thermodynamics: The thermodynamics based on average behavior of large groups of individual particles is called statistical thermodynamics. In this case, the laws of classical mechanics are not applicable and special laws for microscopic systems are successfully applied.

The distinction between application of classical and statistical thermodynamics is done by calculating dependence of mass density with volume of system. A curve is drawn which shows the reasons in which either of the thermodynamics is applicable i.e. when the variation of mass density with volume is

negligible the classical thermodynamic provides accurate results.

Power: The rate of energy transfer is said to be power. Unit: Watt (W)

Ideal gas: It is theoretical gas composed of a set of randomly moving, non-interacting point particles. It obeys the ideal gas law given by PV = nRT

Where V = total volume, n = number of moles of the gas

P = total pressure , T = absolute temperature

R = universal gas constant

The ideal gas law is a limiting law that is valid primarily for gaseous systems at low pressure.For practical purposes, it is observed to remain valid at atmospheric pressures also.Hence, it serves as a useful approximation for the estimation of all real fluid thermodynamic properties of practical interest.

Force:A force is any interaction, that when unopposed will changed the motion of an object i.e. it can caused a body to change it velocity (eg. Can stop moving object or set a stationary object into motion). Newton's second law of motion is generally used to defined force. While Newton's (N) is SI unit of force, kgf and lbf are most commonly used units of pressure.

$1N = 1\ kg\ (m/s^2)$

$1\ lbf = 32.174\ lb_m\ (ft/s^2)$

$1\ kgf = 9.81\ kg\ (m/s^2)$

Pressure: It is the normal force exerted by a system against unit area of the boundary surface.It's unit in SI system is Pascal (Pa), which is the force of one Newton acting on an area of $1m^2$.

$1Pa = 1\ N/m^2$

$1\ bar = 10^5$ Pascal = 100kPa = 0.1MPa

and standard atmospheric pressure, 1atm = 101.325kPa

Gauge Pressure: The pressure relative to the atmosphere is said to be gauge pressure.

Atmospheric pressure: The atmospheric air exerts a normal pressure upon all surfaces with which it is in contact.

Vacuum Pressure: The pressure below atmospheric pressure i.e. negative orange pressure.

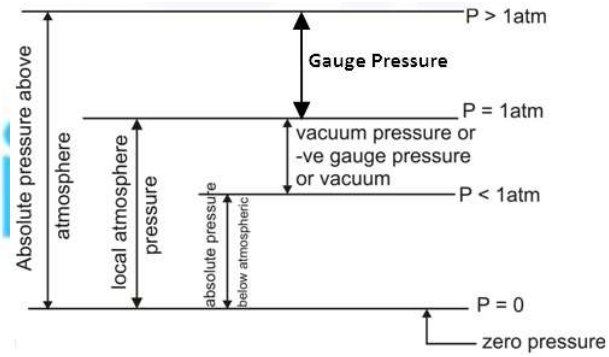

Fig. 1.9. Diagrammatic representation of commonly used pressures

1mm of Hg = 1 torr = 133.322 Pascal

1.4. The phase Rule:

The phase rule determines the number of independent variables that must specified to establish the intensive state of any system at Equillibrium. For reactive system:

F = C – P + 2 – r – s

F = Degree of freedom of thermodynamic system

C = Number of components

P = Number of co-existing phases

r = Number of independent reactions that may occur between the system component

s = Special constraint (mentioned data)

For a non-reactive system

$F = C - P + 2$

Phase refers to solid, liquid or gas.

Various phases can coexist, but they must be in Equillibrium for the phase rule to apply.Component refers to the number of pure substances present in system.Consider a biphasic system of a pure component–say water and steam. There comes only 1 degree of freedom.i.e. either temperature or pressure may be specified to fix all other intensive properties of the system.

Example: Calculate the number of degrees of freedom when a liquid solution of alcohol in water is in Equillibrium with its vapour.

$F = C - P + 2$

Component = 2 (alcohol, water)

Phase = 2 (liquid, vapour)

$\therefore F = 2$

Variables are temperature, pressure and phase compositions. Fixing the mole fraction of water in liquid phase automatically fixes the mole fraction of alcohol.

Questions and Solutions

1. Convert the following readings of pressure to kPa, assuming that the barometer reads 760 mm of Hg.

(a) 40 cm Hg vacuum

(b) 90 cm Hg gauge

(c) 1.2 m of H_2O gauge

Solution:

(a) $P_{vacuum} = h\rho g = (40\times10^{-2})\times(13.6\times10^{3})\times9.8$

$= 53.31 \times 10^3$ N/m^2 = 53.31 kPa

$P_{absolute} = P_{atm} - P_{vacuum}$

$= (760 - 400) \times 9.8 \times 13.6 \times 10^3$

$= 48 \times 10^3$ N/m^2 = 48 kPa

(b) $P_{gauge} = h\rho g = (90 \times 10^{-2}) \times (13.6 \times 10^3) \times 9.8$

$= 120 \times 10^3$ N/m^2 = 120 kPa

Since P_{atm} = 760 mm Hg = 101.325 kPa

$P_{absolute} = P_{gauge} + P_{atm}$

= 120 + 101.325 = 221.325 kPa

(c) $P_{gauge} = h\rho g = 1.2 \times 1000 \times 9.81$

= 11.772 kPa

$P_{absolute}$ = 11.772 + 101.325 = 113.097 kPa

2. Acceleration is sometimes measured in g's, or multiples of the standard acceleration of gravity. Determine the net upward force that an astronaut whose mass is 68 kg experiences if the acceleration on lift-off is 10 g's.

Solution:

Net vertical force

$F_{net} = F = mg = ma$

A = 10 × 9.806 = 98.06 m/s^2

F = 68 × 98.06 = 6668 N