

## BASIC

## THERMODYNAMICS

MECHANICAL ENGINEERING

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GATE-2019: Basic Thermodynamics | Detailed theory with GATE \& ESE previous year papers and detailed solu ons.
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## CHAPTER - 1 <br> BASIC CONCEPTS

### 1.1 INTRODUCTION

Thermodynamics is a combination of two words: thermo+dynamics where thermo: heat and dynamics: power it can be called as the science which deals with energy conversion form one from to another from like heat to power.
It can deals with energy interactions between system and surrounding. Excellently it is also defined as the science of three E's: Equilibrium, Energy and Entropy. It is based four laws: Zeroth law, First law, Second law and Third law.
Whereas, the principles of thermodynamics one can derive general relations between such quantities as coefficients of expansion, compressibility, specific heat capacities, heats of transformation, and magnetic and dielectric coefficients.
The thermodynamics is basically used to design energy conversion devices like: Boiler, Turbine, Compress, Heat exchanger etc.
Thermodynamics is an experimental science based on a small number of principles that are generalizations made from experience. It is concerned only with macroscopic or large-scale properties of matter and it makes no hypotheses about the small-scale or microscopic structure of matter.

## 1. In Microscopic Thermodynamics

The behavior of the gas is described by summing up the behavior of each molecule. It may be calculated by the statistical techniques.

## 2. In Macroscopic Thermodynamics

The behavior of the gas is described by the net effect of action of all the molecules, which can be observed by human senses. It may be calculated by the classical techniques.

### 1.2 EQUILIBRIUM

It is a state in which the system is not capable of finite spontaneous change to another state without a finite change in the state of the surroundings or the state where spontaneous changes does not occur. It may classified as:

## 1. Mechanical Equilibrium

It attains with equality of Pressure in any system.

## 2. Thermal Equilibrium

It attains with equality of Temperature in any system.

## 3. Chemical Equilibrium

It attains with equality of Chemical potential in any system.

## 4. Thermodynamic Equilibrium

When there is no change in any macroscopic property, if system is isolated from its surroundings. A system will be in a state of thermodynamic equilibrium if the system will be in Mechanical, Thermal and Chemical Equilibrium.


1. The volume and temperature of air (assumed to be an ideal gas) in a closed vessel is $2.87 \mathrm{~m}^{3}$ ans 300 K , respectively. The gauge pressue indicated by manometer fitted to the wall of the vessel is $0.5 b a r$. If the gas constant of air is $\mathrm{R}=$ $287 \mathrm{~J} / \mathrm{KgK}$ and yhe atmospheric presure is 1bar, the mass of air(in Kg ) in the vessel is
[GATE - 2017]
(a) 1.67
(b) 3.33
(c) 5.00
(d) 6.66
2. Assuming constant temperature condition and air to be an ideal gas, the variation in atmospheric pressure with height calculated from fluid statics is.
(a) Linear
(b) Exponential
(c) Quadratic
(d) Cubic
3. The internal energy of an ideal gas is a function of
[GATE - 2016]
(a) Temperature and pressure
(b) Volume and pressure
(c) Entropy pressure
(d) Temperature only
4. Temperature of nitrogen in a vessel of volume $2 \mathrm{~m}^{3}$ is 288 K . A U-tube manometer connected by the vessel shows a reading of 70 cm of mercury (level higher in the end open to atmosphere). The universal gas constant is 8314 $\mathrm{J} / \mathrm{kmol}-\mathrm{K}$, atmospheric pressure is 1.01325 bar , acceleration due to gravity is $9.81 \mathrm{~m} / \mathrm{s}^{2}$ and density of mercury is $13600 \mathrm{~kg} / \mathrm{m}^{3}$. The mass of nitrogen (in kg ) in the vessel is
[GATE - 2015]
5. A mixture of ideal gases has the following composition by mass:


If the universal gas constant is $8314 \mathrm{~J} / \mathrm{kmol}-\mathrm{K}$, the characteristic gas constant of the mixture (in $\mathrm{J} / \mathrm{kg}-\mathrm{K}$ ) is $\qquad$
[GATE - 2015]
6. The Van der Waals equation of state is $\left(\mathrm{p}+\frac{\mathrm{q}}{\mathrm{v}^{2}}\right)(\mathrm{v}-\mathrm{b})=\mathrm{RT}$ where p is pressure, v is specific volume, T is temperature and R is characteristic gas constant. The SI unit of a is
[GATE - 2015]
(a) $\mathrm{J} / \mathrm{kg}-\mathrm{K}$
(b) $\mathrm{m}^{3} / \mathrm{kg}$
(c) $\mathrm{m}^{5} / \mathrm{kg}-\mathrm{s}^{2}$
(d) $\mathrm{Pa} / \mathrm{kg}$
7. A certain amount of an ideal gas is initially at a pressure $P$ and temperature $T_{1}$. First, it undergoes a constant pressure process 1-2 such that $\mathrm{T}_{2}=3 \mathrm{~T}_{1} / 4$. Then, it undergoes a constant volume process $2-3$ such that $T_{3}=T_{1} / 2$. The ratio of the final volume to the ideal gas is
[GATE - 2014]
(a) 0.25
(b) 0.75
(c) 1.0
(d) 1.5
8. A pure substance at 8 MPa and $400^{\circ} \mathrm{C}$ is having a specific internal energy of $2864 \mathrm{~kJ} / \mathrm{kg}$ and a specific volume of $0.03432 \mathrm{~m}^{3} / \mathrm{kg}$. Its specific enthalpy (in $\mathrm{kJ} / \mathrm{kg}$ ) is
[GATE - 2014]
9. An isolated thermodynamic system executes a process, choose the correct statement(s) form the following
[GATE - 1999]
(a) No heat is transferred
(b) No work is done
(c) No mass flows across the boundary of the system
(d) No chemical reaction takes place within the system

## 10. Match List-I with List-II <br> List I

## CHAPTER - 2

WORK AND HEAT TRANSFER

### 2.1 INTRODUCTION

A closed system and its surroundings can interact in two ways:

1. By work transfer
2. By heat transfer

Also known as Energy Interactions and these bring about changes in the properties of the system. Heat and work are form of energy.

### 2.2 SIMILARITIES BETWEEN HEAT AND WORK

Similarities between Heat and Work as discussed below:

1. Both exist in transit state.
2. Both referred as Boundary phenomenon.
3. Both are path functions.
4. Both are inexact differentials denoted by symbol delta. ( $\delta \mathrm{Q} / \mathrm{dQ}$ or $\delta \mathrm{W} \mathrm{Dw}$ )

### 2.3 DISSIMILARITIES BETWEEN HEAT AND WORK

Dissimilarities between Heat and Work as discussed in table below:

| Heat | Work |
| :--- | :--- |
| Heat can only be transferred when there is <br> difference of temperature between the system <br> and surroundings. | Work transfer can measured in terms of <br> displacement in the surroundings. |
| Heat is low grade energy. | Work is high grade energy. |
| Heat can transfers under stable or unstable <br> condition. | Work cannot transfer under stable system. |

The concept of either heat transfer or work transfer can be understand with following consideration:


Heat Transfer

Heating plate


Work Transfer

When gas considered as system the energy which cross the boundary due to temperature difference takes place between gas and surrounding. The energy which transfers due to temperature difference is called as heat transfer.
When heating plate considered as system the electrical energy cross the boundary of system which is considered as work transfer.


1. An engine operates on the reversible cycle as shown in the figure. The work output from the engine (in $\mathrm{kJ} / \mathrm{cycle}$ ) is $\qquad$ (correct to two decimal places).

[GATE - 2018]
2. Air is held inside a non-insulated cylinder using a piston (mass $\mathrm{M}=25 \mathrm{~kg}$ and area $\mathrm{A}=$ $100 \mathrm{~cm}^{2}$ ) and stoppers (of negligible area), as shown in the figure. The initial pressure $\mathrm{P}_{1}$ and temperature $\mathrm{T}_{1}$ of air inside the cylinder are 200 kPa and $400^{\circ} \mathrm{C}$, respectively. The ambient pressure $\mathrm{P}_{\infty}$ and temperature $\mathrm{T}_{\infty}$ are 100 kPa and $27^{\circ} \mathrm{C}$ respectively. The temperature of the air inside the cylinder $\left({ }^{\circ} \mathrm{C}\right)$ at which the piston will begin to move is $\qquad$ (correct to two decimal places).

[GATE - 2018]
3. Which of the following statements are TRUE with respect to heat and work?
(i) They are boundary phenomena
(ii) They are excact differentials
(iii) They are path functions required for the process (in kJ ) is shown in the figure.

$\qquad$
4. Heat and work are
(a) Intensive properties
(b) Extensive Properties
(c) Point functions
(d) Path functions
(a) Both (i) and (ii)
(b) Both (i) and (iii)
(c) Both (ii) and (iii)
(d) Only (iii)
5. An ideal gas undergoes a reversible process in which the pressure varies linearly with volume. The conditions at the start (subscript 1) and at the end (subscript 2) of the process with usual notation are: $\mathrm{p}_{1}=100 \mathrm{kPa}, \mathrm{V}_{1}=0.2 \mathrm{~m}^{3}$ and $\mathrm{p}_{2}=$ $200 \mathrm{kPa}, \mathrm{V}_{2}=0.1 \mathrm{~m}^{3}$ and the gas constant, $\mathrm{R}=$ $0.275 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$. The magnitude of the work
$\qquad$ .
[GATE - 2016]
6. Heat is removed from a molten metal of mass 2 kg at a constant rate of 10 kW till it is completely solidified. The cooling curve is

Assuming uniform temperature throughout the volume of the metal during solidification, the latent heat of fusion of the metal (in $\mathrm{kJ} / \mathrm{kg}$ ) is
[GATE - 2015]
[GATE - 2011]
7. The contents of a well-insulated tank are hated by a resistor of $23 \Omega$ in which 10 A current is flowing. Consider the tank along with its contents as a thermodynamic system. The work done by the system and the heat transfer to the system are positive. The rates of heat (Q), work

## CHAPTER - 3

## ZEROTH LAW OF THERMODYNAMICS

### 3.1 INTRODUCTION TO TEMPERATURE

Temperature may be defined as:

1. Degree of hotness and coldness of a body on a definite scale.
2. Driving force or potential causing the flow of energy as heat.
3. Measure of the mean kinetic energy of the molecules of the system.
4. Determination of parameter like thermal equilibrium for two different systems.

If two systems are equal in temperature, since there will be no change occurs in any property when they brought into communication is called equality of temperature.

### 3.2 ZEROTH LAW OF THERMODYNAMICS

When two systems attain thermal equilibrium with third system, they in turn have equality of temperature with each other.

1. Zeroth law provides the basis of the measurement of temperature of a system.
2. Temperature measuring device is thermometer
3. To measuring of temperature with accuracy and precision is called thermometry.


### 3.3 THERMOMETRIC PROPERTY

A property which changes in valve as a function of temperature is called the thermometric property. The substance which has the thermometric property is called the thermometric substance.

| Thermometers | Thermometric Properties |
| :--- | :--- |
| Liquid thermometer | Length |
| Constant volume gas thermometer | Pressure |
| Constant pressure gas thermometer | Volume |
| Electric resistance thermometer | Resistance |
| Thermocouple | Thermal e.m.f |
| Radiation pyrometer | Thermal radiation |
| Optical pyrometer | Monochromatic radiation |
| Pyrometric cone | Fusion |

### 3.4 TEMPERATURE SCALES

A quantitative measure of the temperature of a system requires reference to some datum plane or reference condition, and the establishment of a suitable temperature unit.


1. The definition of 1 K as per the internationally accepted temperature scale is
[GATE - 1994]
(a) $1 / 100^{\text {th }}$ the difference between normal boiling point and normal freezing point of water (b) $1 / 273.15^{\text {th }}$ 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) $1 / 273.16^{\text {th }}$ of the triple point of water

Sol. (d)

## CHAPTER - 4

FIRST LAW OF THERMODYNAMICS

### 4.1 INTRODUCTION

Joule conducted number of experiments involving different types of work interactions, and found that the work expended was proportional to increase in thermal energy.
Thus,

$$
\mathrm{Q} \propto \mathrm{~W}
$$



### 4.1.1 Examples of Energy Transformations

1. The heat of fuel input to an internal combustion engine can be accounted for as output in the form of mechanical energy and heat loss to cooling medium and surroundings etc.
2. After brakes applied on running vehicle, it brought to rest. The Kinetic energy of the brake leathers converted into heat energy through friction.
3. The conversion of energy also takes place during a current flow through a resistance.

### 4.2 FIRST LAW OF THERMODYNAMICS

First law of thermodynamics stipulates that:

1. Energy can neither be created nor destroyed; it can change from one kind to another or it always conserved.
2. For isolated system; total energy remains constant in its all forms.
3. Energy never vanishes; it has ability that- all the energy goes into a system comes out in some other form of energy.
4. No machine can produce energy with zero expenditure of energy.
5. Energy cannot appear from nothing, nor can it convert into nothing.

### 4.2.1 First law for Cyclic Process

A cyclic process is; if the initial and final states of the system executing the process are identical.

1. Cyclic integral of heat $\oint \partial \mathrm{Q}$ is equal to cyclic integral of work $\oint \partial \mathrm{W}$.
2. If a system is taken through a cycle of processes so that it returns to the same state or condition from which it started, the sum of heat and work effects will be zero.

## CHAPTER - 5

## SECOND LAW OF THERMODYNAMICS

### 5.1 INTRODUCTION

There are some limitations of first law of thermodynamics which stated as follows:

1. First law fixes the exchange rate between heat and work, and places no restrictions on the direction of change.
2. Processes proceed spontaneously in certain directions, but the reverse is not automatically attainable even though the reversal of the processes does not violate the first law.
3. First law provides a necessary but not a sufficient condition for a process to occur, and there does exist some directional law which would tell whether a particular process occurs or not. Answer is provided by the second law of thermodynamics.
For engineering purposes, the second law is best expressed in terms of the conditions which govern the production of work by a thermodynamic system operating cycle.

### 5.2 THERMAL ENERGY RESERVOIR (TER)

A thermal energy reservoir is a large body of infinite heat capacity, which is capable of absorbing or rejecting an unlimited quantity of heat without changing its thermodynamic properties.

### 5.2.1 Source

It is the thermal energy reservoir from which heat $Q$ (say) is absorbed by the system. A source may or may not be at constant temperature where fuel is continuously burn.


### 5.2.2 Sink

It is a thermal energy reservoir to which heat $Q^{\prime}$ is rejected from the system during a cycle. A typically sink is a river or sea or the atmosphere itself.


### 5.3 MECHANICAL ENERGY RESERVOIR (MER)

A mechanical energy thermal reservoir is a large body enclosed by an adiabatic wall which is capable of storing work as potential energy or kinetic energy. It receives and delivers mechanical energy quasi-statically.


1. A heat pump absorbs 10 kW of heat from outside environment at 250 K while absorbing 15 kW of work. It delivers the heat to a room that must be kept warm at 300 K . The coefficient of performance(COP) of the heat pump is $\qquad$
[GATE - 2017]
2. The heat removal rate from a refrigerated space and the power input to the compressor are 7.2 kW and 1.8 kW , respectively. The coefficient of performance (COP) of the refrigerator is $\qquad$ -.
[GATE - 2016]
3. A reversible cycle receives 40 kJ of heat from one heat source at a temp[erature of $127^{\circ} \mathrm{C}$ and 37 kJ from another heat source at $97^{\circ} \mathrm{C}$. The heat rejected (in kJ ) to the heat $\operatorname{sink}$ at $47^{\circ} \mathrm{C}$ is
$\qquad$ -
[GATE - 2016]
4. A Carnot engine (CE-1) works between two temperature reservoirs A and B , where $\mathrm{T}_{\mathrm{A}}=900$ K and $\mathrm{T}_{\mathrm{B}}=500 \mathrm{~K}$. A second Carnot engine (CE-2) works between temperature reservoirs $B$ and C , where $\mathrm{T}_{\mathrm{C}}=300 \mathrm{~K}$. In each cycle of CE-1 and CE-2, all the heat rejected by CE-1 to reservoir B is used by CE-2. For one cycle of operation, if the net Q absorbed by CE-1 from reservoir A is 150 MJ , the net heat rejected to reservoir C by CE-2 (in MJ ) is
[GATE - 2015]
5. The COP of a Carnot heat pump operating between $6^{\circ} \mathrm{C}$ and $37^{\circ} \mathrm{C}$ is $\qquad$
[GATE - 2015]
6. Two identical metal blocks $L$ and $M$ (Specific heat $=0.4 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}$ ), each having a mass of 5 kg , are initially at 313 K . A reversible refrigerator extracts heat from block L and rejects heat to block M until the temperature of block $L$ reaches 293 K . The final temperature(in K ) of block M is $\qquad$ -.
[GATE - 2014]
7. A reversible heat engine receives 2 kJ of heat form a reservoir at 1000 K and a certain amount of heat form a reservoir at 800 K . It rejects 1 kJ of heat to a reservoir at 400 K . the net work output (in kJ ) of the cycle is
[GATE - 2014]
(a) 0.8
(b) 1.0
(c) 1.4
(d) 2.0
8. A source at a temperature of 500 K provides 1000 kJ of heat. The temperature of environment in $27^{\circ} \mathrm{C}$. The maximum useful work (in kJ ) that can be obtained from the heat source is $\qquad$
[GATE - 2014]
9. Which one of the following pairs of equations describes an irreversible heat engine?
[GATE - 2014]
(a) $\oint \delta \mathrm{Q}>0$ and $\oint \frac{\delta \mathrm{Q}}{\mathrm{T}}<0$
(b) $\oint \delta Q<0$ and $\oint \frac{\delta Q}{T}<0$
(c) $\oint \delta Q>0$ and $\oint \frac{\delta Q}{T}>0$
(d) $\oint \delta Q<0$ and $\oint \frac{\delta Q}{T}>0$
10. Consider the following two processes;
[GATE - 2010]
Process-I: A heat source at 1200 K loses 2500
kJ of heat to a sink at 800 K
Process-II: A heat source at 800 K loses 2000
kJ of heat to a sink at 500 K
Which of the following statements is ture?
(a) Process I is more irreversible than Process II
(b) Process II is more irreversible than Porcess I
(c) Irreversibility associated in both the
processes are equal
(d) Both the processes are reversible

## CHAPTER - 6

ENTROPY AND AVAILABILITY

### 6.1 INTRODUCTION

The cyclic integral of quantity $\oint_{\mathrm{R}} \frac{\delta \mathrm{Q}}{\mathrm{T}}=0$ for reversible process is zero. Where the quantity $\frac{\delta \mathrm{Q}}{\mathrm{T}}$ represent a point function and it is a property of the system. This property of the system called as entropy $(S)$ and its change from initial to final state during a reversible process is:
$\int_{i}^{f}\left(\frac{\delta Q}{T}\right)_{R}=\int_{i}^{f} d S=S_{f}-S_{i}$
Unit of entropy is $\mathrm{kJ} / \mathrm{K}$ and for specific entropy is $\mathrm{kJ} / \mathrm{kgK}$. The entropy can be measured due to molecule disorder or molecular randomness. As the system becomes more disorder higher will be the entropy.

For a reversible adiabatic process $\delta Q=0$ and so the entropy change will be zero. It clearly stated that entropy is a property of the system that remains constant during a reversible adiabatic process. The reversible adiabatic process during which entropy remains constant is called isentropic process.

1. The entropy for process can be negative, positive and zero.
2. The net entropy for a system can never be less than zero.
3. $\mathrm{S}_{\mathrm{gas}}>\mathrm{S}_{\text {liquid }}>\mathrm{S}_{\text {solid }}$
4. Entropy for pure crystal is always zero at 0 K .
5. Every isentropic process can never be reversible adiabatic process

### 6.2 ENTROPY IS A POINT FUNCTION

Consider a system taken from initial sate $i$ to final state $f$ by following the reversible path $A$. subsequently the system may be brought back to initial state by following the reversible paths B or C.

The paths A and B or A and C individually constitutes a reversible cycle. Then accordance with clausius theorem:



1. An ideal gas undergoes a process from state 1 $\left(\mathrm{T}_{1}=300 \mathrm{~K}, \mathrm{p}_{1}=100 \mathrm{kPa}\right)$ to state $2\left(\mathrm{~T}_{2}=600\right.$ $\left.\mathrm{K}, \mathrm{p}_{2}=500 \mathrm{kPa}\right)$. The specific heats of the ideal gas are : $\mathrm{C}_{\mathrm{p}}=1 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$ and $\mathrm{C}_{\mathrm{v}}=0.7 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$. The change is specific entropy of the ideal gas from state 1 to state 2 (in $\mathrm{kJ} / \mathrm{kg}-\mathrm{K}$ ) is (correct to two decimal places)
[GATE - 2018]
2. For an ideal gas with constant properties undergoing a quasi - static process, which one of the following represents the chge of entropy $(\Delta s)$ from state 1 or 2 ?
[GATE - 2018]
(a) $\Delta \mathrm{s}=\mathrm{C}_{\mathrm{p}} \ln \left(\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}\right)-\mathrm{R} \ln \left(\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}}\right)$
(b) $\Delta \mathrm{s}=\mathrm{C}_{\mathrm{v}} \ln \left(\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}\right)-\mathrm{R} \ln \left(\frac{\mathrm{V}_{2}}{\mathrm{~V}_{1}}\right)$
(c) $\Delta \mathrm{s}=\mathrm{C}_{\mathrm{p}} \ln \left(\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}\right)-\mathrm{C}_{\mathrm{v}} \ln \left(\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}}\right)$
(d) $\Delta \mathrm{s}=\mathrm{C}_{\mathrm{v}} \ln \left(\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}\right)+\mathrm{R} \ln \left(\frac{\mathrm{V}_{1}}{\mathrm{~V}_{2}}\right)$
3. One kg of an ideal gas(gas constant, $\mathrm{R}=$ $400 \mathrm{~J} / \mathrm{kgK}$; specific heat at constant volume, $\mathrm{c}_{\mathrm{v}}=$ $1000 \mathrm{~L} / \mathrm{Kg} . \mathrm{K})$ at 1 bar , and 300 K is contained in a sealed rigid cylinder. During an adiabatic process, 100 kJ of work is done on the system by a stirrer. The increase in entropy of the system is $\qquad$ J/K.
[GATE - 2017]
4. One kg of an ideal gas(gas constant $\mathrm{R}=$ $287 \mathrm{~J} / \mathrm{Kg} . \mathrm{K}$ ) undergoes an irreversible process from state-1 (1bar, 300 K ) to state-2(2bar, 300 K ). The change inspecific entropy $\left(s_{2}-s_{1}\right)$ of the gas $(\mathrm{n} \mathrm{J} / \mathrm{kg} . \mathrm{K})$ in the process is $\qquad$ .
[GATE - 2017]
5. A closed system contains 10 kg of saturated liquid ammonia at $10^{\circ} \mathrm{C}$. Heat addition required to convert the entire liquid into saturated vapour at a constant pressure is 16.2 MJ . If the entropy of the saturated liquid is $0.88 \mathrm{~kJ} / \mathrm{kg} . \mathrm{K}$, the entropy (in $\mathrm{kJ} / \mathrm{kg} . \mathrm{K}$ ) of saturated vapour is
[GATE - 2014]
6. An amount of 100 kW of heat is transferred through a wall in steady state. One side of the wall is maintained at $127^{\circ} \mathrm{C}$ and the other side at $27^{\circ} \mathrm{C}$. The entropy generated (in $\mathrm{W} / \mathrm{K}$ ) due to the heat transfer through the wall is $\qquad$ .
[GATE - 2014]
7. The maximum theoretical work obtainable, when a system interacts to equilibrium with a reference environment, is called
[GATE - 2014]
(a) Entropy
(b) Enthalpy
(c) Exergy
(d) Rothalpy
8. The pressure, temperature and velocity of air flowing in pipe are $5 \mathrm{bar}, 500 \mathrm{~K}$ and $50 \mathrm{~m} / \mathrm{s}$, respectively. The specific heats of air at a constant pressure and at constant volume are $1.005 \mathrm{~kJ} / \mathrm{kgK}$ and $0.718 \mathrm{~kJ} / \mathrm{kgK}$, respectively. Neglect potential energy. If the pressure and temperature of the surroundings are 1 bar and 300 K , respectively, the available energy in $\mathrm{kJ} / \mathrm{kg}$ of the air stream is
[GATE - 2013]
(a) 170
(b) 187
(c) 191
(d) 213
9. An ideal gas of mass $m$ and temperature $T_{1}$ undergoes a reversible isothermal process from an initial pressure $P_{1}$ to final pressure $P_{2}$. The heat loss during the process is Q . The entropy change $\Delta \mathrm{S}$ of the gas is
[GATE - 2012]

## CHAPTER - 7

## THERMODYNAMIC PROPERTY RELATIONS

### 7.1 INTRODUCTION

The thermodynamic property pressure ( P ), volume ( V ), temperature $(\mathrm{T})$ and mass can be easily possible to measure but the properties like: internal energy, enthalpy and entropy cannot measure directly however the properties like density and specific volume can be easily determined by using some specific relations. Thus, it is necessary to drive some fundamental relation between commonly used thermodynamic properties.

### 7.2 PARTIAL DIFFERENTIAL RELATION

Consider of function that depends on two (or more) variables, such as $z=z(x, y)$. It represents the value of $z$ depends upon both $x$ and $y$.
The total differential of $y$ can be written as:
$d z=\left(\frac{\partial z}{\partial x}\right)_{y} d x+\left(\frac{\partial z}{\partial y}\right)_{x} d y$
$d z=M d x+N d y$
where $\mathrm{M}=\left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}}$ and $\mathrm{N}=\left(\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}}$
Taking partial derivative of M and N with respect to y and x respectively. We get,
$\left(\frac{\partial M}{\partial y}\right)_{x}=\frac{\partial^{2} z}{\partial x \partial y}$ and $\left(\frac{\partial N}{\partial x}\right)_{y}=\frac{\partial^{2} z}{\partial y \partial x}$
$\left(\frac{\partial \mathrm{M}}{\partial \mathrm{y}}\right)_{\mathrm{x}}=\left(\frac{\partial \mathrm{N}}{\partial \mathrm{x}}\right)_{\mathrm{y}}$
This is important relation for partial derivatives, and it is commonly used in calculus to check weather differential dz is exact or inexact.
In thermodynamic the above relation helps to form Maxwell relations.

### 7.2.1 Reciprocity and cyclic relation

The function $\mathrm{z}=\mathrm{z}(\mathrm{x}, \mathrm{y})$ can also be expressed as $\mathrm{x}=\mathrm{x}(\mathrm{y}, \mathrm{z})$ if y and z are taken to be independent variables.
The total differential of x can be written as:

$$
d x=\left(\frac{\partial x}{\partial y}\right)_{z} d y+\left(\frac{\partial x}{\partial z}\right)_{y} d z
$$

Put equation (iii) into equation (i) to eliminate $d x$ from equation (i),

$$
\begin{aligned}
& d z=\left(\frac{\partial z}{\partial x}\right)_{y}\left[\left(\frac{\partial x}{\partial y}\right)_{z} d y+\left(\frac{\partial x}{\partial z}\right)_{y} d z\right]+\left(\frac{\partial z}{\partial y}\right)_{x} d y \\
& d z=\left(\frac{\partial z}{\partial x}\right)_{y}\left(\frac{\partial x}{\partial y}\right)_{z} d y+\left(\frac{\partial z}{\partial y}\right)_{x} d y+\left(\frac{\partial z}{\partial x}\right)_{y}\left(\frac{\partial x}{\partial z}\right)_{y} d z
\end{aligned}
$$

## GATE QUESTIONS

1. A tank of volume $0.05 \mathrm{~m}^{3}$ contains a mixture of saturated water and saturated steam at $200^{\circ} \mathrm{C}$. the mass of the liquid present is 8 kg . the entropy (in $\mathrm{kJ} / \mathrm{kg} \mathrm{K}$ ) of the mixture is (correct of two decimal places) Property data for saturated steam and water are: At $200^{\circ} \mathrm{C}, \mathrm{P}_{\text {sat }}=1.5538 \mathrm{MPa}$
$\mathrm{V}_{\mathrm{f}}=0.001157 \mathrm{~m}^{3} / \mathrm{kg}, \mathrm{V}_{\mathrm{t}}=0.12736 \mathrm{~m}^{3} / \mathrm{kg}$
$\mathrm{S}_{\mathrm{fg}}=4.1014 \mathrm{~kJ} / \mathrm{kgK}, \mathrm{S}_{\mathrm{f}}=2.3309 \mathrm{~kJ} / \mathrm{kgK}$
[GATE - 2018]
2. For water at $25^{\circ} \mathrm{C}, \mathrm{dp}_{\mathrm{s}} / \mathrm{dT}_{\mathrm{s}}=0.189 \mathrm{kPa} / \mathrm{K}\left(\mathrm{p}_{\mathrm{s}}\right.$ is the saturation pressure in kPa and $\mathrm{T}_{\mathrm{s}}$ is the saturation temperature in K ) and the specific volume of dry saturated vapour is $43.38 \mathrm{~m}^{3} / \mathrm{kg}$. Assume that the specific volume of liquid is negligible in comparson with that of vapour. Using the Clasius-Calpeyron equation, estimate of the enthalpy of evaporation of water at $25^{\circ} \mathrm{C}$ (in $\mathrm{kJ} / \mathrm{kg}$ ) is $\qquad$
[GATE - 2016]

Sol. 1. ( $2.49 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$ )
Total volume of $\operatorname{tank}(\mathrm{V})=0.05 \mathrm{~m}^{3}$ Means of liquid $\left(\mathrm{m}_{2}\right)=8 \mathrm{~kg}$

$x=\frac{m_{v}}{m_{v}+m_{L}}$ (dryness fraction)
$\mathrm{V}=\mathrm{V}_{\mathrm{L}}+\mathrm{V}_{\mathrm{V}} \quad\left[\begin{array}{l}\mathrm{V}_{\mathrm{L}}-\mathrm{v} \text { of liquid in tank } \\ \mathrm{V}_{\mathrm{V}}-\mathrm{v} \text { of vapour in tank }\end{array}\right]$
$\mathrm{V}_{\mathrm{V}}=\mathrm{m}_{\mathrm{v}} \mathrm{v}_{\mathrm{v}}$
$\mathrm{V}_{\mathrm{V}}=@ 200^{\circ} \mathrm{C}$
$=0.12736 \mathrm{~m}^{3} / \mathrm{kg}$
$\mathrm{V}_{\mathrm{V}}=\mathrm{m}_{\mathrm{L}} \mathrm{V}_{\mathrm{L}}$
$\mathrm{V}_{\mathrm{L}}=\mathrm{v}_{\mathrm{f}} @ 200^{\circ} \mathrm{C}$
$=0.00157 \mathrm{~m}^{3} / \mathrm{kg}$
$\mathrm{V}_{\mathrm{L}}=8 \times 0.00157=9.256 \times 10^{3} \mathrm{~m}^{3}$
$0.05=9.256 \times 10^{-3}+\mathrm{V}_{\mathrm{V}}$
$\mathrm{V}_{\mathrm{v}}=0.0474 \mathrm{~m}^{3}$
So, $0.04074=\mathrm{m}_{\mathrm{v}} \times 0.12736$
$\mathrm{M}_{\mathrm{v}}=0.3198 \mathrm{~kg}$
$\mathrm{x}=\frac{0.3198}{0.3198+8}$
$\Rightarrow \quad \mathrm{x}=0.0384$
Specific entropy of mixture (s)
$\mathrm{S}=\mathrm{S}_{\mathrm{f}}+\mathrm{xS} \mathrm{S}_{\mathrm{fg}}$
$\mathrm{S}=2.3309+0.0384+4.1014$
$\mathrm{S}=2.4884 \mathrm{~kJ} / \mathrm{kg}-\mathrm{K}$
Sol. 2. ( 2443.25 kJ/kg)
$\frac{\mathrm{dP}_{\mathrm{s}}}{\mathrm{dT}_{\mathrm{s}}}=0.189 \frac{\mathrm{kPa}}{\mathrm{K}}$
$\mathrm{T}_{\text {sat }}=275 \mathrm{c}+25=298 \mathrm{~K}$
$\mathrm{V}_{\mathrm{g}}=43.38 \mathrm{~m}^{3} / \mathrm{kg}$
$\mathrm{V}_{\mathrm{f}}=0$
$\mathrm{V}_{\mathrm{fg}}=\mathrm{V}_{\mathrm{g}}-\mathrm{V}_{\mathrm{f}}$
$=43.38-0=43.38 \mathrm{~m}^{3} / \mathrm{kg}$
$\frac{\mathrm{dP}}{\mathrm{dT}}=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{T}_{\mathrm{sat}} \times \mathrm{V}_{\mathrm{fg}}}$
$0.189=\frac{\mathrm{h}_{\mathrm{fg}}}{\mathrm{T}_{\text {sat }} \times \mathrm{V}_{\mathrm{fg}}}=\frac{\mathrm{h}_{\mathrm{fg}}}{298 \times 43.38}$
$\mathrm{h}_{\mathrm{fg}}=2443.25 \mathrm{~kJ} / \mathrm{kg}$

## IAS OBJ QUESTIONS

1. According to the Maxwell's relation, which of the following is/are correct?
[IAS - 2007]
(a) $\left(\frac{\partial \mathrm{v}}{\partial \mathrm{T}}\right)_{\mathrm{P}}=-\left(\frac{\partial \mathrm{s}}{\partial \mathrm{P}}\right)_{\mathrm{T}}$
(b) $\left(\frac{\partial \mathrm{s}}{\partial \mathrm{v}}\right)_{\mathrm{T}}=\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$
(c) $\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}=\left(\frac{\partial \mathrm{s}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$
(d) All of the above
2. Which one of the following is the correct statement?
Clapeyron Equation is used for
[IAS - 2007]
(a) Finding specific volume of vapour
(b) Finding specific volume of liquid
(c) Finding latent heat of vaporization
(d) Finding sensible heat
3. For an ideal gas the expression $\left[\mathrm{T}\left(\frac{\partial \mathrm{s}}{\partial \mathrm{T}}\right)_{\mathrm{P}}-\mathrm{T}\left(\frac{\partial \mathrm{s}}{\partial \mathrm{T}}\right)_{\mathrm{v}}\right]$ is always equal to
[IAS - 2003]
(a) Zero
(b) $\frac{c_{p}}{c_{v}}$
(c) R
(d) RT
4. Assertion (A): Water will freeze at a higher temperature if the pressure is increased.
Reason (R): Water expands on freezing which by Clapeyron's equation gives negative slope for the melting curve.
[IAS - 2003]
Of these statements
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not a correct explanation of A
(c) A is true but R is false
(d) A is false but R is true
5. Match List-I with List-II and select the correct answer using the codes given below the lists.

## List-I

A. Joule Thomson co-efficient
B. $\mathrm{C}_{\mathrm{P}}$ for mono atomic gas
C. $\mathrm{C}_{\mathrm{p}}-\mathrm{C}_{\mathrm{v}}$ for diatomic gas
D. $\left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$

## List-II

(i) $\frac{5}{2} R$
(ii) $\mathrm{C}_{\mathrm{V}}$
(iii) R
(iv) $\left(\frac{\partial T}{\partial P}\right)_{h}$
[IAS - 2002]
Codes:
(a) A-iii,B-ii,C-iv,D-i
(b) A-iv,B-i,C-iii,D-ii
(c) A-iii,B-i,C-iv,D-ii
(d) A-iv,B-ii,C-iii,D-i
6. The specific heat $C_{P}$ is given by
[IAS - 2000]
(a) $T\left(\frac{\partial v}{\partial T}\right)_{P}$
(b) $\mathrm{T}\left(\frac{\partial \mathrm{T}}{\partial \mathrm{S}}\right)_{\mathrm{P}}$
(c) $T\left(\frac{\partial s}{\partial T}\right)_{P}$
(d) $\mathrm{T}\left(\frac{\partial \mathrm{T}}{\partial \mathrm{v}}\right)_{\mathrm{P}}$
7. Match List-I with List-II and select the correct answer using the codes given below the lists

## List-I

A. Mechanical work
B. $\int \frac{\mathrm{dQ}}{\mathrm{T}} \leq 0$
C. Zeroth Law
D. H-TS

