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E-mail: **info@neerajbooks.com**
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Price
₹ 240/-

Published by:

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Sales Office : **1507, 1st Floor, Nai Sarak, Delhi-110 006**

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CONTENTS

THERMODYNAMICS AND STATISTICAL MECHANICS

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Sample Preview of the Solved Sample Question Papers

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QUESTION PAPER

(June – 2017)

(Solved)

THERMODYNAMICS AND STATISTICAL MECHANICS

Time: 2 Hours] *[Maximum Marks: 50*

Note: ***All*** *questions are* ***compulsory****. Marks alloted for each questions are indicated against it. You can use log tables or non-programmable calculators. Symbols have their usual meaning.*

Q. 1. Attempt any *three* parts:

(a) **What are isotherms and adiabats? Show that the slope of an adiabat is $\gamma\ (=C_p/C_v)$ times the slope of an isotherm.**

Ans. A non-mathematical way to look at it is to realise that isothermal means constant temperature. If you increase the pressure then heat energy must be removed to make the change isothermal.

Isothermal process is given by PV = constant

In adiabats chnage no heat energy is allowed to enter OV leave the system. So in an adiabatic compression the temperature of the gas will increase which provides an additional increase in pressure.

Adiabatic process is given by PV^r = constant.

Also Add. Ref.: See Chapter-4, Page No. 52, 'Ratio of adiabat and Isothermal Elasticities'.

(b) **Draw T-S diagram for a Carnot cycle. Calculate efficiency of a Carnot engine.**

Ans. Ref.: See Chapter-5, Page No. 71, Q. No. 2.

(c) **Define mean free path. Obtain the expression for survival equation.**

Ans. Mean Free Path: The mean free path is the average distance travelled by a moving particle between successive impacts (collision). It is denoted by symbol λ

If λ_1 , λ_2 , λ_3 ..... λ_n are successive true path transversed in time t and N is the total number of collisions then.

$$\lambda = \frac{\lambda_1 + \lambda_2 + ... + \lambda_n}{n}$$

$$= \frac{\bar{v}t}{N}$$

where $\bar{v}$ is average speed of molecules.

$\tau = t/N$ denoted the mean time between two successive collisions then we can write.

$$\lambda = \bar{v}\tau = \frac{\bar{v}}{P_c}$$

where $P_c = \tau^{-1}$ denotes the collision frequency molecules suffer collision very frequently and mean free path hence all value fro zero to infinity.

(d) **Starting from the expression**

$$\mathbf{W} = \prod_i \frac{\mathbf{g}_i}{(\mathbf{g}_i - \mathbf{N}_i)!\mathbf{N}!}$$

show that the distribution function for a Fermi-Dirac system is given by

$$f(\in) = \frac{1}{e\beta(\in - \mu) + 1}$$

Sol. We know $W = \prod \frac{g_i}{(g_i - N_i)!N!}$

The multiplicity function for the whole system is

the product at the multiplicity function and given as:

$$W = \prod_i W_i$$

if N be total no of electron in a system and exists of N electrons is equal to $\in$.

$$N = \sum_i g_i f_i\ .$$

According to hangrange method of under terminal multiplication.

$$\partial\omega = a\sum_j g_i f_i - b\sum_j \in_i g_i f_i$$

$$\log \frac{g_i - g_i f_i}{g_i f_i} - abf_i > 0$$

$$f_\in - f_\mu = \frac{2.27\times10^7 \text{ J}}{373\text{K}}$$

if $\beta = \frac{1}{B}$ and comparing with dv–Tds – Pdv + Mdv.

then

$$f(\in) = \frac{1}{1+e\beta(\in-\mu)}$$

Q. 2. 1 kg of water is heated from 0°C to 100°C and converted into steam at the same temperature. Calculate the increase in entropy, given that specific heat of water is 4.18×10^3 J kg^{-1} K^{-1} and latent heat of vaporisation is 2.27×10^7 J kg^{-1}.

Ans. $\partial\theta = ml$

$m = 1$ kg

$l = 2.27 \times 10^7$ J kg^{-1}

$$\partial\theta = 2.27\times10^7\times1$$

$$\partial\theta = 2.27\times10^7\times\text{J}$$

$$\partial s = \frac{\partial\theta}{\text{T}} = \frac{2.27\times10^7\text{ J}}{373\text{K}}$$

$$\partial s = 60.85\times10^3\text{ JK}^{-1}$$

Or

A mass *m* of a liquid at temperature T_1 is mixed with an equal mass of the same liquid at temperature T_2. The system is thermally insulated. Show that the change in entropy is

$$\Delta S = 2mC_p \ln\left[\frac{(T_1+T_2)}{2\sqrt{T_1T_2}}\right].$$

Ans. Ref.: See Chapter-5, Page No. 69, Q. No. 3.

Q. 3. Attempt any *two* parts:

***(a)* The initial temperature of a gas is 27°C. Calculate the rise in temperature when it is compressed suddenly to 10 times its original pressure (γ = 1.5).**

Sol. P_1 = P atm

P2 = 10 P atm

$y = 1.5$

$T_1 = 27°$C

$T_2 = ?$

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right) y - \frac{1}{y}$$

$$T_2 = T_1\left(\frac{P_1}{P_2}\right) 1.5 - \frac{1}{1.5}$$

$$T_2 = 27\left(\frac{1}{10}\right)1.5 - .66$$

$$T_2 = 27\left(\frac{1}{10}\right) = 27\times\left(\frac{1}{10}\right)^{-29}$$

$$T_2 = \frac{27}{10} = 2.7°\text{k}$$

***(b)* What are bosons and fermions? Give at least two examples of each. Of the two isotopes of helium, ^{3}He and ^{4}He, which one is boson and which one is fermion? Justify your conclusion.**

Ans. Ref.: See Chapter-15, Page No. 165, Q. No. 3.

***(c)* What is Brownian motion? Discuss its significance for kinetic theory of gases. How did Perrin use mean square displacement of a Brownian particle to weigh a nitrogen molecule?**

Ans. Brownian motion is also known as Brownian movement. Brownian motion any of various physical phenomena in which some quantity is constantly undergoing small, and random fluctuations.

Examples of Brownian Motion:

1. Sedimentation or pollutants in atmosphere.
2. Motion of galvanometer mirror.
3. Johnson Noise

Perrin used to determine Avogadro's number was to measure the root square displacement of grains during certain successive equal time intervals.

The expression Perrin used to determine Avogadro's number in a combination of Einstein's equation for the root mean square displacement in one dimension and the expression for the diffusion coefficient and has the form.

$$N = \frac{t\,RT}{<\eta^2> 3\pi a\varepsilon^{-1}}$$

Where N Avogadro's number, t time is solved $<\eta^2>$ the root mean square displacement of R is gas Constant a be the radius of the grain T is temperature and ε is viscosity of fluid.

Sample Preview
of
The Chapter

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Thermodynamics and Statistical Mechanics

The Zeroth Law and The First Law

Basic Concepts of Thermodynamics

1

INTRODUCTION

The laws of thermodynamics are observed regularly every day. You often see someone using a bicycle pump to inflate the tyre of his bicycle. And you observe that the pump through which you inflat the tyre gets hot. Consider the experience of being in a small crowded room with lots of other people. In all likelihood, you'll start to feel very warm and will start sweating. This is the process your body uses to cool itself off. Heat from your body is transferred to the sweat. As the sweat absorbs more and more heat, it evaporates from your body, becoming more disordered and transferring heat to the air, which heats up the air temperature of the room. Another such example is rubbing your hands. When you rub your both hands you feel warmth. All these examples show that the heating is arised as a result of the mechanical work done in the compressing the gas pump or pushing the hand to move against friction. These show the relation between mechanical and thermal effects which is known as thermodynamics.

The word "thermodynamic" is derived from two Greek words *thermes*, meaning heat, and *dynamikos*, meaning powerful. Thermodynamics states a set of four laws that are valid for all systems that fall within the constraints implied by each.

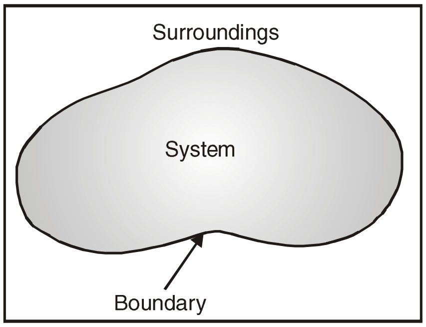
The study of thermodynamics is based on four empirical laws. The first law of thermodynamics is the law of conservation of energy and matter. Energy can neither be created nor destroyed; it can however be transformed from one form to another. The second law states that isolated systems gravitate towards thermodynamic equilibrium, also known as a state of maximum entropy, or disorder; it also states that heat energy will flow from an area of low temperature to an area of high temperature. These laws are observed regularly every day. Let us understand by one more example:

Every day, ice needs to be maintained at a temperature below the freezing point of water to remain solid. On hot summer days, however, people often take out a tray of ice to cool beverages. In the process, they witness the first and second laws of thermodynamics. For example, someone might put an ice cube into a glass of warm lemonade and then forget to drink the beverage. An hour or two later, they will notice that the ice has melted but the temperature of the lemonade has cooled. This is because the total amount of heat in the system has remained the same, but has just gravitated towards equilibrium, where both the former ice cube (now water) and the lemonade are the same temperature. This is, of course, not a completely closed system. The lemonade will eventually become warm again, as heat from the environment is transferred to the glass and its contents.

CHAPTER AT A GLANCE

THERMODYNAMIC SYSTEMS

A thermodynamic system is the content of a macroscopic volume in space, along with its walls and surroundings; it undergoes thermodynamic processes according to the principles of thermodynamics. A primary goal of the study of thermochemistry is to determine the quantity of heat exchanged between a system and its surroundings. The system is the part of the universe being studied, while the surroundings are the rest of the universe that interacts with the system. Every system is enclosed by an arbitrary surface which is called its boundary, and the reason of space lies outside the boundary of a system is called its surroundings.



A system and its surroundings can be as large as the rain forests in South America or as small as the contents of a beaker in a chemistry laboratory. The type of system one is dealing with can have very important implications in chemistry because the type of system dictates certain conditions and laws of thermodynamics associated with that system.

Boundary sectors are of various characters: rigid, flexible, fixed, moveable, actually restrictive and fictive or not actually restrictive. For example, in an engine, a fixed boundary sector means the piston is locked at its position; then no pressure-volume work is done across it. In that same engine, a moveable boundary allows the piston to move in and out, permitting pressure-volume work. There is no restrictive boundary sector for the whole earth including its atmosphere, and so roughly speaking, no pressure-volume work is done on or by the whole earth system. Such a system is sometimes said to be diabatically heated or cooled by radiation.

For example, if we are studying the engine of the vehicle, in this case engine is called as the system. Similarly, the other examples of system are refrigerator, air-conditioner, washing machine, heat exchange, a utensil with hot water, etc. The system is covered by the boundary and the area beyond the boundary is called as universe or surroundings. The boundary of the system can be fixed or it can be movable. Between the system and surrounding the exchange of mass or energy or both can occur.

Classification of Systems

Systems may be classified as Closed System, Open System and Isolated System. Let's describe one by one below:

Closed System

A closed system consists of a fixed amount of mass. The system in which the transfer of energy takes place across its boundary with the surrounding, but no transfer of mass takes place is called as closed system. The closed system is fixed mass system. The fluid like air or gas being compressed in the piston and cylinder arrangement is an example of the closed system. In this case the mass of the gas remains constant but it can get heated or cooled. Another example is the water being heated in the closed vessel, where water will get heated but its mass will remain same.

Open System

An open system is a system that freely exchanges energy and matter with its surroundings. The system in which the transfer of mass as well as energy can take place across its boundary is called as an open system. Our previous example of engine is an open system. In this case we provide fuel to engine and it produces power which is given out, thus there is exchange of mass as well as energy. The engine also emits heat which is exchanged with the surroundings. The other example of open system is boiling water in an open vessel, where transfer of heat as well as mass in the form of steam takes place between the vessel and surroundings.

Isolated System

The system in which neither the transfer of mass nor that of energy takes place across its boundary with the surroundings is called as isolated system. For example if the piston and cylinder arrangement in which the fluid like air or gas is being compressed or expanded is insulated it becomes isolated system. Here, there will neither transfer of mass nor that of energy.

Similarly hot water, coffee or tea kept in the thermos flask is closed system. However, if we pour this fluid in a cup, it becomes an open system.

Classification of Boundaries

1. Diathermal Boundary: If the heat can exchange flow with the surroundings, is called diathermal. In other words, one that does permit the flow of heat is called diathermal. For examples, a copper wall and a metallic tea pot provide a diathermal boundary to its contents. Another example is a metallic tea pot which provides a diathermal boundary to its content.

2. Adiabatic Boundary: It is the boundary which refers to the conditions under which overall heat transfer across the boundary between the thermodynamic system and the surroundings is absent. It means it does not permit any heat to flow across the boundary. For example, the walls of an ideal thermos flask is an example of adiabatic boundary. The flow of a viscous liquid or gas through a heat-insulated channel is often referred to as adiabatic.

3. Rigid Boundary: Rigid boundary is the boundary which cannot be moved by an external force. A system having such a boundary can neither be compressed nor expanded. Hence, a rigid boundary does not permit the volume of the system to change.

4. Permeable Boundary: A boundary which allows exchange of matter is called permeable boundary.

5. Semi-permeable boundary: A boundary that restricts the flow of some kinds of particles, while allowing others to cross is known as semi-permeable boundary. For example, hot quartz allows helium to flow but restricts other gases.

THERMODYNAMICS STATE OF A SYSTEM AND THERMODYNAMICS VARIABLES

A key concept in thermodynamics is the state of a system. A thermodynamic state of a system is fully identified by values of a suitable set of parameters known as state variables, state parameters or thermodynamic variables.

The word State refers to the condition of a system as described by its properties. Since there are normally relations among the properties of a system, the state often can be specified by providing the values of a subset of the properties. All other properties can be determined in terms of these few. Consider a system not under going any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition, or the state, of the system. At a given state, all the properties of a system have fixed values. If the value of even one property changes, the state will change to a different one.

There are other thermodynamic variables: temperature T, entropy S, and internal energy U. These will be discussed later; they are common to all thermodynamic systems. Thermodynamic variables can be divided into two groups: extensive variables and intensive variables. Let us know about them.

Intensive and Extensive Variables

Consider two bodies each with the same volume V_1 group and the same pressure. Bring the bodies together, what is the result? Variables that are additive like V_1 group are called extensive variables, they depend on the size or the extent of the system. Variables that do no add, but combine like P group are called intensive variables, they are intrinsic to the system and can vary from point to point. Fields and potentials are intensive variables. Hence, an extensive property of a system does depend on the system size or the amount of material in the system. Examples of extensive properties include: Mass, volume, entropy, enthalpy, energy, stiffness, etc.

Intensive variable is one that does not depend on the volume of the system, and an extensive variable is one that does. An intensive quantity (also intensive variable) is a physical quantity whose value does not depend on the amount of the substance for which it is measured. Intensive property is also known as Bulk Property. Examples of intensive properties include: Temperature, chemical potential, density, specific gravity, viscosity, velocity and electrical resistivity.

Thermodynamic Equilibrium

Let us suppose that there are two bodies at different temperatures, one hot and one cold. When these two bodies are brought in physical contact with each other, temperature of both the bodies will change. The hot body will tend to become colder while the cold body will tend to become hotter. Eventually, both the bodies will achieve the same temperatures and they are said to be in thermodynamic equilibrium with each other.

In an isolated system when there is no change in the macroscopic property of the system like entropy, internal energy etc, it is said to be in thermodynamic equilibrium. The state of the system which is in thermodynamic equilibrium is determined by intensive properties such as temperature, pressure, volume, etc.

Whenever the system is in thermodynamic equilibrium, it tends to remain in this state infinitely and will not change spontaneously. Thus, when the system is in thermodynamic equilibrium there won't be any spontaneous change in its macroscopic properties.

The best example of the thermodynamic equilibrium would be: A certain mass of hot oil kept in a metallic container sealed from all sides, hot oil will attain thermal equilibrium with metal. Mechanical equilibrium is already present due to equally shaped container and chemical equilibrium is their as their is no reaction of other elements on metal due to oil.

THERMODYNAMIC PROCESSES

When the system undergoes a change from its initial state to the final state, the system is said to have undergone a process. During the thermodynamic process, one or more of the properties of the system like temperature, pressure, volume, enthalpy or heat, entropy, etc. changes. The second law of thermodynamics enables us to classify all the processes under two main categories: reversible or ideal processes and irreversible or natural processes.

Let us understand by an example, the expansion of a gas in a cylinder at constant pressure due to heating, is a thermodynamic process. Another example, suppose a wire is stretched tightly, between two rigid supports. It has certain tension and length. Now, if this wire is allowed to cool it would shrink. Since, the wire is not permitted to shrink, a tension is developed in the wire to stretch it. So it will have a diferent tension and length, and will be said to have executed a thermodynamic process.

Reversible and Irreversible Processes

A process is called irreversible if the system and all parts of its surroundings cannot be exactly restored to their respective initial states after the process has occurred. A system that has undergone an irreversible process is not necessarily precluded from being restored to its initial state. However, were the system restored to its initial state, it would not be possible also to return the surroundings to the state they were in initially.

Consider an isolated system. The second law says that any process that would reduce the entropy of the isolated system is impossible. Suppose, a process takes place within the isolated system in what we shall call the forward direction. If the change in state of the system is such that the entropy increases for the forward process, then for the backward process (that is, for the reverse change in state) the entropy would decrease. The backward process is therefore impossible, and we therefore say that the forward process is irreversible.

If a process occurs, however, in which the entropy is unchanged by the forward process, then it would also be unchanged by the reverse process. Such a process could go in either direction without contradicting the second law. Processes of this latter type are called reversible.

The key idea of a reversible process is that it does not produce any entropy. Entropy is produced in irreversible processes. All real processes (with the possible exception of superconducting current flows) are in some measure irreversible, though many processes can be analyzed quite adequately by assuming that they are reversible. Some processes that are clearly irreversible include: mixing of two gases, spontaneous combustion, friction, and the transfer of energy as heat from a body at high temperature to a body at low temperature.

Consider a sample of gas inside a piston cylinder (a cylinder with one movable end cap so the volume inside the piston can be changed). The gas evenly fills the volume of the cylinder (the defining property of gases). Let it understand by an example, If the cylinder full of gas is fitted with a piston, the volume occupied by the gas is V. On the piston the weight W is placed in such a manner that its removal of the piston takes up the position A'B' and 2V becomes the volume of the gas. Now consider you want to increase the volume of the gas to 2V, you can increase it by removing W, this is irreversible process because it takes place quickly.

Hence, processes involving other kinds of spontaneous events are irreversible, such as an unrestrained expansion of a gas or liquid considered in Figure below. Friction, electrical resistance, hysteresis, and inelastic deformation are examples of effects whose presence during a process renders it irreversible.

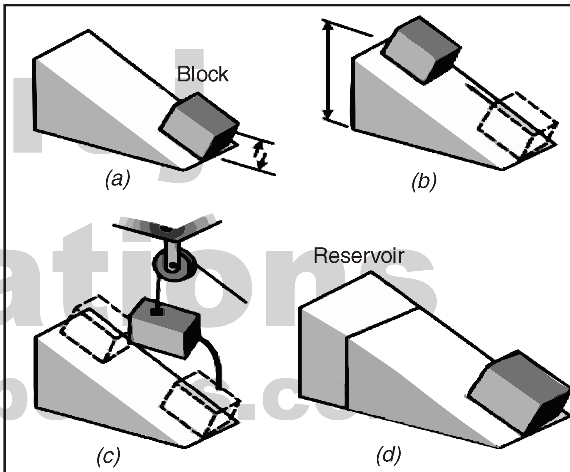


Figure used to demonstrate the irreversibility of a process involving friction

You must note that a system that undergoes an irreversible process may still be capable of returning to its initial state; however, the impossibility occurs in restoring the environment to its own initial conditions. An irreversible process increases the entropy of the universe. However, because entropy is a state function, the change in entropy of a system is the same whether the process is reversible or irreversible. The second law of thermodynamics can be used to determine whether a process is reversible or not.

For example, water flows from high level to low level, current moves from high potential to low potential, etc. Here, are some important points about the irreversible process: