Name of Paper : Thermal Physics and Statistical Mechanics
Name of the Course : B.Sc. (Prog.) II Year (CBCS)
Semester : III
Duration : 3 Hours
Maximum Marks : 75

2021

Attempt any four questions of this questions paper
Each question is of 18.75 marks.

Q. 1. (*a*) Define extensive and intensive variables with the help of examples. Explain how first leads to the concept of internal energy and law of thermodynamics. (8)

Sol. Extensive variables : If the value of a thermodynamic variable depends on the size of the system, then it is said to be an extensive quantity. The values of extensive quantities depend on the number of atoms (mols) that are present in the system. Examples – Volume, strain, entropy etc.

Intensive variables : If the value of a thermodynamic variable does not depend on the size of the system, then it is said to be an intensive quantity. The values of intensive quantities do not depend on the number of atoms (mols) that are present in the system. Examples – Temperature, pressure, magnetic field intensity etc.

Internal energy and First law of thermodynamics

Internal energy is the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest. Thus, it includes only the (disordered) energy associated with the random motion of molecules of the system. We denote the internal energy of a system by U. Internal energy U of a system is an example of a thermodynamic 'state variable' – its value depends only on the given state of the system, not on history i.e. not on the 'path' taken to arrive at that state.

The internal energy U of a system can change through two modes of energy transfer: heat and work.

Let ΔQ = Heat supplied to the system by the surroundings
ΔW = Work done by the system on the surroundings
ΔU = Change in internal energy of the system

The general principle of conservation of energy then implies that $\Delta Q = \Delta U + \Delta W$ (1) i.e. the energy (ΔQ) supplied to the system goes in partly to increase the internal energy of the system (ΔU) and the rest in work on the environment (ΔW). Equation (1) is known as the First Law of Thermodynamics. It is simply the general law of conservation of energy applied to any system in which the energy transfer from or to the surroundings is taken into account.

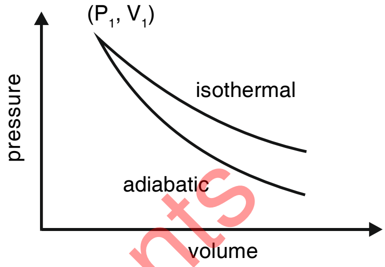
ideal gas. Why is P – V curve for adiabatic process steeper than that for isothermal process. **(5)**

Sol. P – V Diagram representing isothermal and adiabatic of an ideal gas

Adiabatic process : PV = constant

$$\therefore \qquad V^{\gamma}dP + {}_{\gamma}PV^{\gamma-1}\,dV = 0$$

$$\therefore \qquad \frac{dP}{dV} = -\frac{\gamma P}{V}$$



Isothermal process : PV = constant

$$\therefore \qquad PdV + VdP = 0$$

$$\therefore \qquad \frac{dP}{dV} = \frac{P}{-V}$$

Now, $\qquad Y > 1$

$$\therefore \qquad \left|\left(\frac{dP}{dV}\right)_{\text{adiabatic}}\right| > \left|\left(\frac{dP}{dV}\right)_{\text{isotherm}}\right|$$

$\therefore \dfrac{dP}{dV}$ is the slope of the P – V curve.

$\therefore$ The P – V curve for an adiabatic process is steeper than that for an isothermal process.

(*c*) Deduce the latent heat question of Clausis $C_2 - C_1 = (dL/dT) - (L/T)$ where C_1 and C_3 represent the specific heat of a liquid and saturated vapour and L is the latent heat of the vapour. **(5.75)**

Sol. Latent heat question of Clausius

$$dS = \frac{\delta Q}{T}$$

The change of entropy *d*S is given by the relation

For a change of state from liquid to vapour at constant temperature T = The boiling points of the liquid, δQ = L, the latent heat of vaporisation. If S_1 is the entropy in the liquid state and S_2 in the vapour state, then

$$dS = S_2 - S_1$$

$$\therefore \qquad S_2 - S_1 = \frac{L}{T} \qquad \text{...(1)}$$

Differentiating equation (1) with respect to T, we have

$$\frac{dS_2}{dT} - \frac{dS_1}{dT} = \frac{L}{T^2} + \frac{1}{T}\frac{dL}{dT}$$

or $$T\frac{dS_2}{dT} - T\frac{dS_1}{dT} = \frac{L}{T} + \frac{dL}{dT}$$

Now $$T\frac{dS_2}{dT} = c_2 \text{ specific heat in the vapour state}$$

and $$T\frac{dS_1}{dT} = c_1 \text{ specific heat in the liquid state}$$

$\therefore$ $$c_2 - c_1 = \frac{dL}{dT} - \frac{L}{T}$$

This is known as Clausius Latent heat equation.

Q. 2. (*a*) State Carnot's theorem and show that it is necessary consequence of second law of thermodynamics. Using Carnot theorem, prove Clausis inequality. (12)

Sol. Carnot theorem state that of all heat engines working between the same (constant) temperature, the reversible Carnot engine has the maximum efficiency. Let us consider an irreversible engine (I) and a reversible engine (R) operating between the same reservoirs which are at temperatures T_1 and T_2. Suppose that the irreversible engine is more efficient than a reversible engine. Then we can write

$$\eta_I > \eta_R$$

Let us consider an irreversible cycle engine working between temperatures T_1 and T_2. If a reversible engine were operating between the same temperature, it follows from Carnot theorem (Sec. 6.4.1), that

$$\eta_{irr} < \eta_{rev}$$

or $$\frac{Q_1^{irr} - Q_2^{irr}}{Q_1^{irr}} < \frac{Q_1^{rev} - Q_2^{rev}}{Q_1^{rev}}$$

This expression can be rearranged as

$$\frac{Q_2^{irr}}{Q_1^{irr}} > \frac{Q_2^{rev}}{Q_1^{rev}} = \frac{T_2}{T_1}$$

or $$\frac{Q_2^{irr}}{T_2} > \frac{Q_1^{irr}}{T_1}$$

$$\oint_{irr} \frac{\delta Q}{T} = \frac{Q_1^{irr}}{T_1} - \frac{Q_2^{irr}}{T_2} < 0 \qquad ...(1)$$

In words, this inequality implies that the value of the cyclic integral $\oint_{irr} \frac{\delta Q}{T}$ will be less than zero for an irreversible process. If we make the engine more an more irreversible, the integral in equation (1) will progressively become smaller and smaller. Thus, for all irreversible heat engine cycles, we can write

$$\oint_{irr} \frac{\delta Q}{T} < 0 \qquad ...(2)$$

On combining equation (2), we find that for heat engines we can, it general, write

$$\oint_{irr} \frac{\delta Q}{T} \leq 0 \qquad ...(3)$$

This relation is known as the Clausius ineqality. Note that the equality holds only for reversible heat engines.

(*b*) There are two Carnot engines A and B operating in two different temperature regions. For Engine A the temperatures of the two reservoirs are 200°C and 150°C. For engine B the temperature of the reservoirs are 300°C and 250°C. Which engine has lesser efficiency? (6.75)

Sol. For Engine A	For Engine B
$T_1 = 200°C$	$T_1 = 300°C$
$T_2 = 150°C$	$T_2 = 250°C$
efficiency of engine A	efficiency of engine B
$\eta_A = 1 - \frac{T_2}{T_1}$	$\eta_B = 1 - \frac{T_2}{T_1}$
$= 1 - \frac{150}{200}$	$= 1 - \frac{250}{300}$
$= 0.25$	$= 0.166$
$\eta_A = 25\%$	$\eta_B = 16.6\%$

$\therefore$ Efficiency of engine B in lesser than engine A $\eta_B < \eta_A$.

thermodynamics in terms of entropy? (6.75)

Sol. Refer question no. 14 [Page no. 16] and question no. 17 [Page no. 19] of chapter 1.

(*b*) Using the Maxwell's law of distribution of molecular speed; derive expression for : (12)

(*i*) Average speed

(*ii*) Most probable speed

(*iii*) Root mean square speed

Sol. (*i*) Average speed using maxwell's law of distribution of molecular speed

$$\therefore \text{ Average velocity (or speed) } \bar{v} = \frac{\int_0^\infty v\, n(v) dv}{\int_0^\infty n(v)\, dv} = \frac{\int_0^\infty v\, n(v) dv}{n}$$

But according to M.B distribution of molecular speeds

$$n(v)\, dv = 4\pi n \left(\frac{m}{2\pi k T}\right)^{3/2} e^{\frac{-m}{2kT}v^2}\ v^2 dv = \frac{4}{\sqrt{\pi}} n\, b^3\ e^{-b^2 v^2}\ v^2 dv$$

where $b = \sqrt{\frac{m}{2kT}}$

$$\therefore \qquad \bar{v} = \frac{1}{n}\frac{4}{\sqrt{\pi}} nb^3 \int_0^\infty e^{-b^2 v^2}\ v^3\ dv$$

Using the standard integral $\int_0^\infty x^3 e^{-ax^2}\ dx = \frac{1}{2a^2}$ we have

$$\int v^3\, e^{-b^2 v^2} dv = \frac{1}{2b^4}$$

Substituting in (*i*) we have

$$\text{Average velocity } \bar{v} = \frac{4}{\sqrt{\pi}} b^3 \frac{1}{2b^4} = \frac{2}{\sqrt{\pi}}\frac{1}{b} = \sqrt{\frac{4\,.\,2kT}{\pi m}} = \sqrt{\frac{8kT}{\pi m}} = 1.59\sqrt{\frac{kT}{m}}\,.$$

Most probable speed (velocity). The most probable velocity $\nu_{m.p}$ is which the number of molecules having that velocity is a maximum.

According to Maxwell-Boltzmann statistics, the number of molecules having speeds) between ν and (ν + *d*ν) is given by

$$n(\nu)\, d\nu = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{\frac{-m}{2kT}}\ \nu^2\, d\nu$$

The total number of molecules $n = \int_0^\infty n(\nu)\, d\nu$

$\therefore$ The proability that a molecule may possess a velocity between ν and (ν + *d*ν) is given by

$$p(\nu)\, d\nu = \frac{n\,(\nu)\, d\nu}{n} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}\nu^2}\ \nu^2\, d\nu$$

$$= \frac{4}{\sqrt{\pi}} b^3\ e^{-b^2\nu^2}\ \nu^2\ d\nu \qquad \text{where} \qquad b = \sqrt{\frac{m}{2kT}}$$

Hence, the probability that a molecule may have a velocity lying in the unit velocity interval $\left(\nu - \frac{1}{2}\right)$ and $\left(\nu + \frac{1}{2}\right)$ around the value ν is given by P(ν)

$$= \frac{4}{\sqrt{\pi}}\, b^3 e^{-b^2\, \nu^2}\ \ \nu^2$$

In order that the probability may be a maximum the expression $\frac{4b^3}{\sqrt{\pi}} e^{-b^2\nu^2}\ \nu^2$ should also be a maximum.

Hence, the condition for most probable velocity is given by

$$\frac{d}{d\nu}\left[\frac{4}{\sqrt{\pi}}\, b^3 e^{-b^2\, \nu^2}\ \ \nu^2\right] = 0$$

or $$\frac{4b^3}{\sqrt{\pi}}\left[2\nu e^{-b^2\nu^2} - \nu^2 e^{-b^2\,\nu^2}\ \ 2b^2\nu\right] = 0$$

or $$\frac{8b^3}{\sqrt{\pi}}\, \nu e^{-b^2\,\nu^2}\ [1 - \nu^2 b^2] = 0 \qquad \text{or} \qquad 1 - \nu^2 b^2 = 0$$

$$\therefore \qquad \nu^2 = \frac{1}{b^2} \text{ or } \nu = \frac{1}{b} = \sqrt{\frac{2kT}{m}}$$

Hence
$$\nu_{m.p} = \sqrt{\frac{2kT}{m}} = 1.41\sqrt{\frac{kT}{m}}$$

(*iii*) Root mean square

$$n(\nu)\,d\nu = 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}\nu^2}\,\nu^2\,d\nu = \frac{4}{\sqrt{\pi}} nb^3\,e^{-b^2\nu^2}\,\nu^2 d\nu$$

where
$$b = \sqrt{\frac{m}{2kT}}$$

Mean or average (velocity)^2

$$= \frac{1}{n}\cdot\frac{4}{\sqrt{\pi}} nb^3\int_0^\infty e^{-b^2\nu^2}\,\nu^4\,d\nu = \frac{4}{\sqrt{\pi}} b^3\int_0^\infty e^{-b^2\nu^2}\,\nu^4\,d\nu$$

Using the standard integral $\int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3}{8}\frac{\sqrt{\pi}}{a^5}$ we

$$\int_0^\infty e^{-b^2\nu^2}\,\nu^4 = \frac{3}{8}\frac{\sqrt{\pi}}{b^5}$$

Substituting in (*i*) we have

$$\text{Mean or average (velocity)}^2 = \frac{4}{\sqrt{\pi}} b^3\,\frac{3}{8}\frac{\sqrt{\pi}}{b^5} = \frac{3}{2}\frac{1}{b^2} = \frac{3}{2}\frac{2kT}{m} = \frac{3kT}{m}$$

The root mean square velocity $\nu_{r.m.s}$ is the square root of mean or average (velocity)^2

$$\therefore \qquad \nu_{r.m.s} = \sqrt{\frac{3kT}{m}} = 1.73\sqrt{\frac{kT}{m}}$$

(*b*) Find the change in entropy when I gram of water at 0°C is converted into steam at 100°C. The specific heat of water is 1 cal/gm °C and latent heat of steam at 100°C is 540 cal/gm. **(6.75)**

Sol. I gm of water at 0°C is heated to 100°C

$$\text{Change in entropy} = 2.3023 \text{ ms} \log_{10}\frac{T_2}{T_1}$$

$$m = \text{mass of water}$$

$$\therefore \qquad \text{Change in entropy} = 2.3026 \times 1 \times 1 \times \log\left(\frac{373}{273}\right)$$

$$= 0.312 \text{ cal/K}$$

I gm of water at 100°C changes to steam at 100°C

$$\text{Change in entropy} = \frac{\delta Q}{T} = \frac{mL}{T}$$

$$L = \text{Latent heat}$$

$$\therefore \qquad \text{Change in entropy} = \frac{1 \times 540}{(273 + 100)} = 1.448 \text{ cal/K}$$

Thus, total change in entropy = 0.312 + 1.448

$$= 1.760 \text{ cal/K.}$$

Q. 5. (*a*) Derive Wein's displacement law and Stefan's law from Planck's radiation law. (10.75)

Sol. Wien's displacement law : The wavelength at which maximum in the curve occurs can be obtained from equation (11.55) using the condition

$$\left[\frac{\partial u_\lambda}{\partial \lambda}\right]_{\lambda = \lambda_{max}} = 0 \qquad (11.58)$$

This leads to

$$\frac{\partial u_\lambda}{\partial \lambda} = 8\pi hc \frac{\partial}{\partial \lambda}\left[\frac{\lambda^{-5}}{\exp(hc/\lambda k_B T) - 1}\right]$$

$$= 8\pi hc \left[\frac{-5\lambda^{-6}\left[\exp(hc/\lambda k_B T) - 1\right] - \lambda^{-5}\left(-\frac{hc}{\lambda^2 k_B T}\exp(hc/\lambda k_B T)\right)}{(\exp(hc/\lambda k_B T) - 1)^2}\right]$$

$$= \frac{8\pi hc}{\lambda^5}\frac{1}{(\exp(hc/\lambda k_B T) - 1)}\left[-\frac{5}{\lambda} + \frac{hc}{\lambda^2 k_B T}\frac{\exp(hc/\lambda k_B T)}{(\exp(hc/\lambda k_B T) - 1)}\right]$$

$$= u_\lambda \left[-\frac{5}{\lambda} + \frac{hc}{\lambda^2 k_B T}\frac{\exp(hc/\lambda k_B T)}{(\exp(hc/\lambda k_B T) - 1)}\right]$$

hand side of the above expression equal to zero put $\lambda = \lambda_{max}$. This gives

Suppose the value of u_λ is maximum for $\lambda = \lambda_{max}$. Therefore, we equate the right-hand side of the above expression equal to zero put $\lambda = \lambda_{max}$. This gives

$$\left[-\frac{5}{\lambda_{max}} + \frac{hc}{\lambda_{max}{}^2 k_B T}\frac{\exp(hc/\lambda_{max}k_B T)}{(\exp(hc/\lambda_{max}k_B T) - 1)}\right] = 0$$

or

$$\frac{hc}{\lambda_{max}k_B T}\frac{\exp(hc/\lambda_{max}k_B T)}{[\exp(hc/\lambda_{max}k_B T) - 1]} = 5 \qquad (11.59)$$

We will now introduce a new variable by defining $x = hc/\lambda_{max}k_B T$. Then we can rewrite equation (11.59) in an elegent from :

$$x\frac{\exp(x)}{\exp(x) - 1} = 5$$

or

$$x = 5\,(1 - e^{-x}) \qquad (11.60)$$

This is a transcendental equation and can be solved graphically or numerically. However, we expect a root in the neighbourhood of 5. By applying the method of approximation, the exact value of x is found to be 4.965. Hence, the result is

$$x = \frac{hc}{\lambda_{max}k_B T} = 4.965$$

Hence,

$$\lambda_{max}T = b = \frac{hc}{k_B \times 4.965} \qquad (11.61)$$

This is Wien's displacement law

On substituting for h, c and k_B, we get

$$\lambda_{max}T = 2.897 \times 10^{-6}\ \text{mK} \qquad (11.62)$$

Stefan's law : The total energy density for photons of all wavelength (frequencies) is obtained by integrating equation (11.57). This gives

$$u(T) = \int_0^\infty u_\lambda d\lambda = 8\pi hc\int_0^\infty \frac{d\lambda}{\lambda^5[\exp(hc/\lambda k_B T) - 1]} \qquad (11.63)$$

To evaluate this integral, we introduce a change of variable by defining $x = \frac{hc}{\lambda k_B T}$ so that $\lambda = \frac{hc}{\lambda k_B T}$ and $d\,\lambda = -\frac{hc}{x^2\,k_B T}dx$. The limits of integration change

$$u(\mathrm{T}) = 8\pi hc \int_{-\infty}^{0} \frac{\left(-\dfrac{hc}{x^2 k_B \mathrm{T}}\right) dx}{\left(\dfrac{hc}{x k_B \mathrm{T}}\right)^5 [\exp(x) - 1]}$$

To absord the negative sign, we change the limits of integration. Hence, we get

$$u(\mathrm{T}) = \frac{8\pi k_B{}^4 \mathrm{T}^4}{c^3 h^3} \int_0^{\infty} \frac{x^3 dx}{\exp(x) - 1}$$

This integral is a standard one and has the value $\Gamma(4)\,\zeta(4) = \pi 4/15$. So, the total energy density at temperature T is given by

$$u(\mathrm{T}) = \frac{8\pi^5 k_B^4}{15 h^3 c^3} \mathrm{T}^4$$

$$= a\mathrm{T}^4 \tag{11.64}$$

where $a = \dfrac{8\pi^5 k_B^4}{15 h^3 c^3} = 7.56 \times 10^{-16}\ \mathrm{Jm}^{3}\mathrm{K}^{-4}$.

If we consider the interior of the Sun as consisting of a photon gas at contant temperature 3×10^6 K, we find that its energy density is equal to

$$u = (7.56 \times 10^{-14}\ \mathrm{Jm}^{-3}\ \mathrm{K}^{-4}) \times (3 \times 106\ \mathrm{K})^4$$

$$= 6.1 \times 10^{10}\ \mathrm{Jm}^{-3}$$

The volume of the sun is nearly equal to 1.4×10^{27} m^3. So, the total energy of photons inside the sun is

$$\mathrm{E} = u\mathrm{V} = 8.6 \times 10^{37}\mathrm{J}$$

If there were a small opening in a cavity, photons will effuse through it. The net rate of flow of radiation per unit area of the opening is given by

$$\mathrm{R} = \frac{1}{4} u\ c = \frac{2\pi^5 k_B^4}{15 h^3\ c^2} \mathrm{T}^4$$

or

$$\mathrm{R} = \sigma \mathrm{T}^4$$

where $\sigma = \dfrac{2\pi^5 k_B^4}{15 h^3\ c^2} = 5.67 \times 10^{-8}\ \mathrm{Jm}^{-2}\mathrm{K}^{-4}s^{-1}$ is Stefan-Boltzmann constant.

law. **(5)**

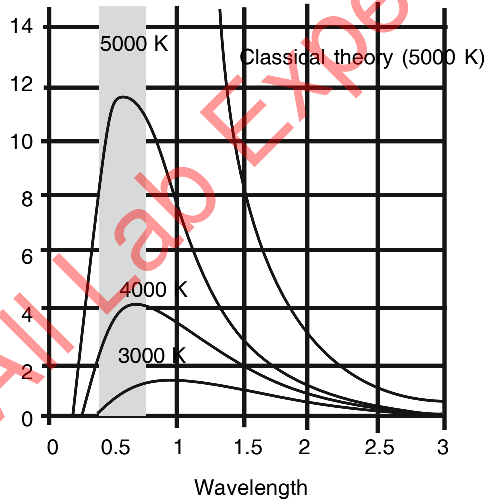
Sol. Ultraviolet Catastrophe : Before **Planck's hypothesis,** physicists tried to describe the spectral radiance of electromagnetic radiation by classical physics. The approximation based on **classical physics** is known as the **Rayleigh-Jeans law**.

Similarly, as for **Planck's law**, the **Rayleigh-Jeans law** gives the spectral radiance of a body as a function of frequency v at absolute temperature T:

$$B_\nu(T) = \frac{2\nu^2 k_B T}{c^2}$$

where

- **$B_\nu(\nu_t T)$** is the spectral radiance (the power per unit solid angle and unit of area normal to the propagation) density of frequency ν radiation per unit frequency at thermal equilibrium at temperature T
- c is the speed of light in a vacuum
- k_g is the Boltzmann constant
- ν is the frequency of the electromagnetic radiation
- T is the absolute temperature of the body



The electromagnetic spectrum predicted by this formula agrees with experimental results at low frequencies (large wavelengths) but strongly **disagrees at high frequencies** (short wavelengths). This inconsistency between observations and the predictions of classical physics is commonly know as the **ultraviolet catestrophe** or **Rayleigh-Jeans catastrophe.** By calculating the total amount of radiant energy (*i.e.*, the sum of emissions in all frequency ranges), it can be shown that a blackbody, in this case, would release an infinite amount of energy, which is in contradiction with the law of conservation of energy.

emits maximum energy of wavelength 550 nm, what would be the temperature of the sun? (3)

Sol. According to wien's displacement law

$$\lambda m\,T = \text{constant}$$

or $$\lambda m_1 T_1 = \lambda m_2 T_2$$

Given $$\lambda m_1 = 2000 \text{ nm} = 2000 \times 10^{-9}\text{m}$$

$$T_1 = 1500k$$

$$\lambda m_2 = 550 \text{ nm} = 550 \times 10^{-9}\text{m}$$

$$T_2 = ?$$

$\therefore$ $$2000 \times 10^{-9} \times 1500 = 550 \times 10^{-9} \times T_2$$

$$T_2 = \frac{2000}{550} \times 1500 = 5454.54\,\text{K}$$

Q. 6. (*a*) Define and explain the terms Macrostate and Microstate with the help of an example.

Sol. Refer Q. 2. **[Page No. 98].**

(*b*) What is meant by the term thermodynamic probability of macrostate? How it is related to probability of occurrence of that state. How does it differ from mathematical probability? (8.75)

Sol. Refer Q. 4. **[Page No. 99].**

(*c*) 4 molecules are to be distributed in 2 cells. Find possible no. of macrostates and corresponding no. of microstates. (4)

Sol. Number of particles $n = 4$

Number of macrostate $= n + 1 = 4 + 1 = 5$

Number of microstates $= 2n = 16$.

OR