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Thermodynamics & Statistical Physics for CSIR-UGC-NET & GATE

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Chapter 1

Basic Introduction

Basics of Thermodynamics

This is the branch of Physics in which we deal with **internal macroscopic state of the system**.

System : Any portion of matter which is considered as **separated from its surrounding** is called system.

Surrounding : All these things which are outside the system and influence its behaviour are known as surrounding.

Example : Let a gas be filled in a cylinder fitted with a piston heated by a burner. Here the gas is the system while the piston and burner are the surroundings.

Thermodynamic system : A thermodynamic system is one which may interact with its surrounding in at least two distinct ways and one of these necessarily a transfer of heat (In or out of the system) and the other may be some other means of transfer of energy say be performance of mechanical work by or on the system through electromagnetic interaction.

Example: Gas contained in a cylinder, vapour in contact with its liquid stretched wire.

Equilibrium : If there is no change in the property of the system w.r.t. time, the system is called in equilibrium.

1. **Mechanical equilibrium** : When there is no unbalanced force interior of the system and between the system and surrounding then the system is in mechanical equilibrium.
Example: Ideal gas inside a container.
2. **Chemical equilibrium** : If the system has no tendency to undergo a change in internal structure and also has no tendency to transfer matter from one part to another part then it is said to be in chemical equilibrium.
3. **Thermal equilibrium**: If there is no temperature difference between any part of the system and also not between the system & surrounding then the system is in thermal equilibrium.
4. **Thermodynamic equilibrium**: A system is said to be in thermodynamical equilibrium if its state doesn't change in any way i.e. mechanical, chemical & thermal equilibrium.

If however the conditions for any one of three type of equilibrium are not satisfied then the system is said to be in non thermodynamic equilibrium. If all are not satisfied then system is called in non-equilibrium.

Microscopic parameter : The parameter of the order of atomic level is called microscopic parameter. There are parameters that describes the internal structure of the system or associated with the constituent of the system. These parameters can't be directly measured in laboratory and can't be experience by our sense of perception.

Example: mass, velocity, energy, momenta, magnetic moment of constituent (atom or molecule) of the system.

Macroscopic parameter: Macroscopic parameter of a system are the average of the sum total of the corresponding microscopic parameter of the constituent particles. These can be measured directly in the laboratory and can be directly experienced by our sense of perception.

Example: pressure, volume, temperature, entropy



Microstate: The state of the system associated with the states of all constituents of the system is called microstate or microscopic state.

Macroscopic State : The state of the system associated with the parameters of the whole system is called macrostate. The macrostate is called thermodynamic state.

A thermodynamic system is taken from initial to final state the work done by the system is given by

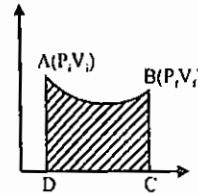
$$dW = FdS = PAdS = PdV$$

$$W = \int_{\text{initial}}^{\text{final}} dW = \int_i^f PdV$$

work done on the system is -ve

work done by the system is +ve

work done = Area under the curve (on PV diagram)

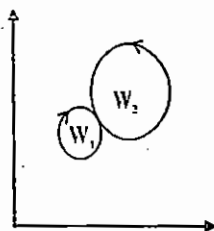
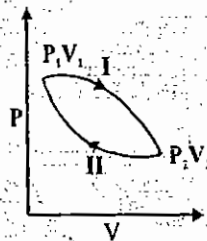


work done depends on the path and can't be written as perfect differential. Similarly, heat also depends on path and can't be written as perfect differential.

P, V, T, U, S are exact or perfect differential (state or point function)

Cyclic Process : When a system undergoes a change from initial state to another final state through different states and come back to initial state then the process is called cyclic process.

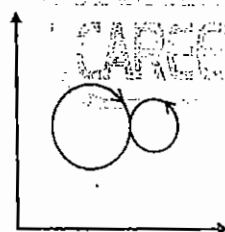
Work done in cyclic process is equal to area enclosed by the cycle. If the cycle is traced anticlockwise work done is -ve i.e. work done on the system. If the cycle is traced clockwise then work done is +ve i.e. work done by the system.



$$W_1 < W_2 \quad W = W_2 - W_1$$

W_2 is anticlockwise
 W_1 is clockwise

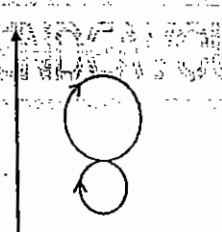
So work done on the system



$$W = W_1 + W_2$$

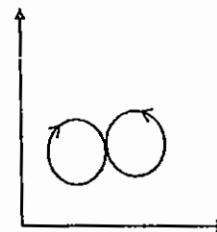
W_1 is clockwise and
 W_2 is anticlockwise

So, work done by the system



$$W = W_1 + W_2$$

W_1 is clockwise and W_2 also
work done by the system



$$W_1 = W_2$$

work done is zero

Internal energy : The internal energy is the energy associated with microscopic mechanical energy

$$I.E. = K.E. + P.E.$$

It is impossible to divide internal energy into a thermal and mechanical part

Let Q be the heat absorbed by the system and W be the work done by the system during the process that leads the system from initial state to final state Q - W is calculated then Q - W is same for different path although Q & W individually are different for different path. Then this is called change in internal energy dU.

$$dU = Q - W$$

Q - W depend only on state (initial and final) and not on the path. The internal energy of a system in a given state is a function of that state only and doesn't at all depend upon the way by which that states has been acquired.



Hence we can't tell whether the internal energy of the system has been acquired by heat transferred or by performance of mechanical work or by both.

The Kinetic Theory of Gases

We can summarize the kinetic theory of gases with four basic postulates:

1. **Gases are made up of molecules:** We can treat molecules as point masses that are perfect spheres. Molecules in a gas are very far apart, so that the space between each individual molecule is many orders of magnitude greater than the diameter of the molecule.
2. **Molecules are in constant random motion:** There is no general pattern governing either the magnitude or direction of the velocity of the molecules in a gas. At any given time, molecules are moving in many different directions at many different speeds.
3. **The movement of molecules is governed by Newton's Laws:** In accordance with Newton's First Law, each molecule moves in a straight line at a steady velocity, not interacting with any of the other molecules except in a collision. In a collision, molecules exert equal and opposite forces on one another.
4. **Molecular collisions are perfectly elastic:** Molecules do not lose any kinetic energy when they collide with one another.

The kinetic theory projects a picture of gases as tiny balls that bounce off one another whenever they come into contact. This is, of course, only an approximation, but it turns out to be a remarkably accurate approximation for how gases behave in the real world. These assumptions allow us to build definitions of temperature and pressure that are based on the mass movement of molecules.

- **Gas Laws**

Boyles Law : $PV = \text{constant}$

Charles Law : $V/T = \text{constant}$

- **Ideal Gas Equation**

$$PV = nRT$$

- **Dalton Law of Partial Pressure**

$$P = P_1 + P_2 + P_3$$

Pressure exerted by n moles of an ideal gas in terms of the speed of the molecules

$$P = \frac{nM(v_{rms})^2}{3V}$$

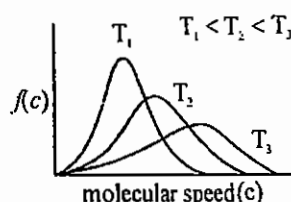
- **Maxwell Speed Distribution Function:**

The number of particle moving with velocity c and $c + dc$ is given by

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mc^2}{2k_B T}} c^2 dc$$

where N is the total number of gas particles and

$$f(c) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mc^2}{2k_B T}} c^2 \text{ is called Maxwell's distribution function.}$$



Average speed, r.m.s speed and most probable speed:



$$\text{Average speed : } \bar{c} = \frac{1}{N} \int_0^{\infty} c dN_c = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\text{R.M.S speed : } c_{rms} = \sqrt{\frac{1}{N} \int_0^{\infty} c^2 dN_c} = \sqrt{\frac{3k_B T}{m}}$$

Most probable speed:

$$\left. \frac{df}{dc} \right|_{c=c_m} = 0$$

$$\text{We get, } c_m = \sqrt{\frac{2k_B T}{m}}$$

$$\bar{c} : c_{rms} : c_m = \sqrt{\frac{8k_B T}{\pi m}} : \sqrt{\frac{3k_B T}{m}} : \sqrt{\frac{2k_B T}{m}}$$

$$\Rightarrow \boxed{c_m : \bar{c} : c_{rms} = 1 : 1.128 : 1.224}$$

Q. Five gas molecules chosen at random are found to have speeds of 500, 600, 700, 800 and 900 m/s? What is the rms speed and average speed?

(a) $v_{rms} = 700$ m/s and $v_{av} = 714$ m/s

(b) $v_{rms} = 71.4$ m/s and $v_{av} = 70.4$ m/s

(c) $v_{rms} = 714$ m/s and $v_{av} = 700$ m/s

(d) $v_{rms} = 70.4$ m/s and $v_{av} = 71.4$ m/s

Soln. Given: $v_1 = 500$ m/s, $v_2 = 600$ m/s, $v_3 = 700$ m/s, $v_4 = 800$ m/s, $v_5 = 900$ m/s

$$v_{avg} = \frac{\sum_{i=1}^5 v_i}{5} = \frac{500 + 600 + 700 + 800 + 900}{5} = 700 \text{ m/s}$$

$$\text{and } v_{rms} = \left(\frac{\sum_{i=1}^5 v_i^2}{5} \right)^{1/2} = \left(\frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5} \right)^{1/2} = 714.14 \text{ m/s}$$

Correct option is (c)

Maxwell's distribution function in momentum and energy form:

The number of particles moving with energy E and $E + dE$ is given by

$$dN_E = 2N \left(\frac{E}{\pi} \right)^{1/2} (k_B T)^{-3/2} e^{-E/k_B T} dE$$

The number of particle moving momentum p and dp is given by

$$dN_p = 4\pi N \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-\frac{p^2}{2m k_B T}} p^2 dp$$



Degree of Freedom

(a) Definition : It is defined as the total number of independent variables required to describe completely the state of motion of a body. It can be calculated as

$$f = 3N - C,$$

where N represents the number of particles [atoms in case of molecules] and C represents the number of constraints [bonds or lone pairs in case of molecules].

Different molecules have various types of degree of freedom corresponds to various types of motion they perform like translation, rotation and vibration. When the molecules are at low temperature, they exhibit only translational motion and hence have only translational degree of freedom. When the temperature increases, they also perform rotational motion along with the translational motion and hence possesses degree of freedom corresponds to both type of motion. When the temperature is sufficiently high, the bonds get weaker and causes the molecules to vibrate along with both translational and rotational motion.

The degree of freedom for various molecules can be calculated as :

(a) For monoatomic molecules [e.g., Ar, Xe, Rn, He].

Each molecule contains one atom and has no bond. So, $N = 1$ and $C = 0$.

Therefore, $f = 3 \times 1 - 0 = 3$.

All these three degree of freedom corresponds to translational degree of freedom.

(b) For diatomic molecules [e.g., O_2 , N_2 , H_2].

Since each diatomic molecule contains two atoms, we have $N = 2$.

(i) At low temperature : The bond between the two atoms remain rigid and hence there is only one constraints.

Therefore, $f = 3 \times 2 - 1 = 5$.

Out of these 5, 3 corresponds to translational motion and 2 corresponds to vibration motion.

(ii) At high temperature : The bond between the atoms do not remain rigid causing the atoms to vibrate as well and hence there is no constraints at high temperature.

Therefore, $f = 3 \times 2 - 0 = 6$.

In this 3 corresponds to translational, 2 corresponds to rotation and the remaining 1 corresponds to vibrational motion.

(c) For linear triatomic molecules [e.g., CO_2 , N_2O].

Since each linear triatomic molecule has three atoms, we have $N = 3$.

(i) At low temperature : Since there are two bonds, the number of constraints will be two.

Therefore, $f = 3 \times 3 - 2 = 7$.

Out of these 7, 3 corresponds to translation, 2 corresponds to rotation [as the molecules are linear] and the remaining 2 are because of vibrational motion. But if the molecules have rigid bonds, these two vibrational degree of freedom are not active.

(ii) At high temperature : The bonds will not remain constraints and hence $C = 0$.

Therefore, $f = 3 \times 3 - 0 = 9$.

Out of these 9, 3 corresponds to translation, 2 corresponds to rotation and the remaining 4 corresponds to vibrational mode.

(d) Non-linear triatomic molecules [e.g., O_3 , H_2O].

Since each non-linear triatomic molecules has three atoms, we have $N = 3$.

(i) At low temperature : The three bonds will behave as three constraints. So, we have

$f = 3 \times 3 - 3 = 6$.

The three, here, corresponds to translational and the remaining three corresponds to rotation [as the molecule is non-linear].

(ii) At high temperature : The bonds will not remain constraints. So, we have

$f = 3 \times 3 - 0 = 9$.



The three will corresponds to translation, three to rotational and the remaining three will corresponds to vibration.

In general, the degree of freedom can be distributed as:

(i) At low temperature:

Types of molecule → Mode ↓	Linear molecule	Non-linear molecule
Translation	3	3
Rotation	2	3
Vibration	$3N - C - 5$	$3N - C - 6$

(ii) At high temperature:

Types of molecule → Mode ↓	Linear molecule	Non-linear molecule
Translation	3	3
Rotation	2	3
Vibration	$3N - 5$	$3N - 6$

Law of Equipartition of Energy

For 1-D, the Maxwell's velocity distribution function is $f(v) = \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv^2}{2k_B T}}$, $-\infty < v < \infty$

So, average kinetic energy is

$$\begin{aligned} \bar{E} &= \frac{\int_{-\infty}^{\infty} E f(v) dv}{\int_{-\infty}^{\infty} f(v) dv} = \frac{\int_{-\infty}^{\infty} \frac{1}{2} m v^2 \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv^2}{2k_B T}} dv}{\int_{-\infty}^{\infty} \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv^2}{2k_B T}} dv} \\ &= \frac{m}{2} \frac{\int_{-\infty}^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv}{\int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_B T}} dv} = \frac{m}{2} \frac{\int_0^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv}{\int_0^{\infty} e^{-\frac{mv^2}{2k_B T}} dv} \end{aligned}$$

Using $\int_0^{\infty} x^n e^{-ax^2} dx = \frac{1}{2} \frac{\Gamma(n+1)}{a^{n/2}}$, we have

$$\Rightarrow \bar{E} = \frac{m \left[\frac{3}{2} / 2 \left(\frac{m}{2k_B T} \right)^{3/2} \right]}{2 \left[\frac{1}{2} / 2 \left(\frac{m}{2k_B T} \right)^{1/2} \right]} = \frac{m}{2} \frac{\frac{1}{2} \sqrt{\pi}}{\sqrt{\pi}} \frac{2k_B T}{m} \Rightarrow \bar{E} = \frac{1}{2} k_B T$$



- (a) **Statement :** In thermal equilibrium, any degree of freedom (such as component of the position or velocity of a particle) which appears only "quadratically" in the energy has an average energy per molecule of

$$\frac{1}{2} k_B T.$$

This is the *law of equipartition of energy*.

- (b) **Examples :**

- (i) **A free particle of mass m moving in xy -plane**

The Hamiltonian will be

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m}$$

Since there are two quadratic terms, the average thermal energy is

$$\langle E \rangle = 2 \times \frac{1}{2} k_B T = k_B T$$

- (ii) **A free particle rotating in xy -plane about z -axis**

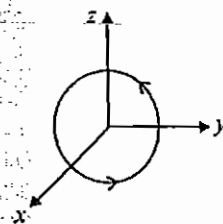
The corresponding Hamiltonian is

$$H = \frac{L_z^2}{2I},$$

where I is the moment of inertia of the particle about z -axis.

Therefore, the average thermal energy is

$$\langle E \rangle = 1 \times \frac{1}{2} k_B T = \frac{1}{2} k_B T$$



- (iii) **A one-dimensional harmonic oscillator in x -axis**

The corresponding Hamiltonian is

$$H = \frac{p_x^2}{2m} + \frac{1}{2} k x^2,$$

where k is the spring's constant.

Therefore, the average thermal energy is

$$\langle E \rangle = 2 \times \frac{1}{2} k_B T = k_B T$$

- (c) **Other statement :** The law of equipartition of energy, therefore, can be re-stated as :

"The average energy corresponds to each translational degree of freedom is $\frac{1}{2} k_B T$, corresponds to each

rotational degree of freedom is $\frac{1}{2} k_B T$ and corresponds to each vibrational degree of freedom is $k_B T$ ".

$$\text{Mathematically, } \langle E \rangle = f_{\text{Translation}} \times \frac{1}{2} k_B T + f_{\text{Rotation}} \times \frac{1}{2} k_B T + f_{\text{Vibration}} \times k_B T.$$

- Q.** Calculate the average thermal energy of a diatomic molecule in both low temperature and high temperature condition.

Soln. (i) At low temperature, we have

$$f_{\text{Translational}} = 3 \text{ and } f_{\text{Rotation}} = 2.$$

$$\text{Therefore, } \langle E \rangle = 3 \times \frac{1}{2} k_B T + 2 \times \frac{1}{2} k_B T = \frac{5}{2} k_B T.$$



(ii) At high temperature, we have

$$f_{\text{Translational}} = 3, f_{\text{Rotation}} = 2 \text{ and } f_{\text{Vibration}} = 1.$$

$$\text{Therefore, } \langle E \rangle = 3 \times \frac{1}{2} k_B T + 2 \times \frac{1}{2} k_B T + 1 \times k_B T = \frac{7}{2} k_B T$$

Note : The formula for average thermal energy per particle as $\langle E \rangle = \frac{f}{2} k_B T$ is valid only when there is no vibrational mode.

Q. A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per O_2 molecule to per N_2 molecule is

- (a) 1 : 1 (b) 1 : 2 (c) 2 : 1
(d) depends on the moment of inertia of the two molecules

Soln. Since both the gases are diatomic, both will have the same number of rotational degree of freedom i.e., two. Therefore, both the gases will have the same average rotational kinetic energy per molecule $= 2 \times \frac{1}{2} k_B T$ or $k_B T$. Thus ratio will be 1 : 1.

Correct option is (a)

Q. A gas mixture consists of 2 moles of oxygen and 4 moles of argon at temperature T . Neglecting all vibrational modes, the total internal energy of the system is

- (a) 4 RT (b) 15 RT (c) 9 RT (d) 11 RT

Soln. Internal energy of n moles of an ideal gas with no vibrational degree of freedom at temperature T is given by

$$U = n \left(\frac{f}{2} RT \right)$$

where, f = degree of freedom.
 $= 5$ for O_2 and 3 for Ar

$$\text{Hence, } U = U_{O_2} + U_{Ar} = 2 \left(\frac{5}{2} RT \right) + 4 \left(\frac{3}{2} RT \right) = 11 RT.$$

Correct option is (d)

Q. In 1-dimension, an ensemble of N classical particles has energy of the form $E = \frac{p_x^2}{2m} + \frac{1}{2} kx^2$. The average internal energy of the system at temperature T is

- (a) $\frac{3}{2} Nk_B T$ (b) $\frac{1}{2} Nk_B T$ (c) $3Nk_B T$ (d) $Nk_B T$

Soln. The given Hamiltonian is

$$E = \frac{p_x^2}{2m} + \frac{1}{2} kx^2$$

According to equipartition theorem, the contribution of each quadratic term in Hamiltonian to average thermal energy is $\frac{1}{2} k_B T$. So the average thermal energy of one particle is

$$U_1 = \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T$$

\therefore Average thermal energy of N -particle system is $U = NU_1 = Nk_B T$

Correct answer is (d)



Q. A classical gas of molecules each of mass m , is in thermal equilibrium at the absolute temperature, T . The velocity components of the molecules along the Cartesian axes are v_x , v_y and v_z . The mean value of $(v_x + v_y)^2$ is:

- (a) $\frac{k_B T}{m}$ (b) $\frac{3 k_B T}{2 m}$ (c) $\frac{1 k_B T}{2 m}$ (d) $\frac{2 k_B T}{m}$

Soln. $\langle (v_x + v_y)^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + 2 \langle v_x v_y \rangle$

Putting $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{k_B T}{m}$ $\left[\because \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) = \frac{3}{2} k_B T \right]$

and $\langle v_x v_y \rangle = 0$

So, $\langle (v_x + v_y)^2 \rangle = \frac{k_B T}{m} + \frac{k_B T}{m} + 0 = \frac{2 k_B T}{m}$

Correct option is (d)

- Vander Waals equation

$$\left(\frac{P + a}{V^2} \right) (V - a) = nRT$$

Mean free path is given by $\lambda = k_B T / \sqrt{2} \pi \sigma^2 P$ (where σ is the diameter of the molecule).

PREVIOUS YEARS SOLUTIONS OF TIFR

Q. Consider the CO molecule as a system of two point particles which has both translational and rotational degrees of freedom. Using classical statistical mechanics, the molar specific heat C_v of CO gas is given in terms of the Boltzmann constant k_B by [TIFR 2014]

- (a) $\frac{5}{2} k_B$ (b) $2 k_B$ (c) $\frac{3}{2} k_B$ (d) $\frac{1}{2} k_B$

Soln. For diatomic molecule, we have

$$f_{\text{translational}} = 3 \text{ and } f_{\text{rotational}} = 2$$

The average energy is

$$\langle U \rangle = \left(\frac{f_{\text{translational}}}{2} + \frac{f_{\text{rotational}}}{2} + f_{\text{vibrational}} \right) \times k_B T = \frac{5}{2} k_B T$$

$$\text{Therefore, } C_v = \frac{d}{dt} \langle U \rangle = \frac{5}{2} k_B$$

Correct option is (a)

Q. Two containers are maintained at the same temperature and are filled with ideal gases whose molecules have mass m_1 and m_2 respectively. The mean speed of molecules of the second gas is 10 times the r.m.s. speed of the molecules of the first gas. Find the ratio of m_1/m_2 to the nearest integer. [TIFR 2016]

Soln. Given : $(v_{\text{mean}})_2 = 10 (v_{\text{r.m.s.}})_1$

$$\Rightarrow \sqrt{\frac{8 k_B T}{\pi m_2}} = 10 \sqrt{\frac{3 k_B T}{m_1}}$$

$$\Rightarrow \frac{m_1}{m_2} = \frac{100 \times 3\pi}{8} = 117.8 \approx 118 \text{ (nearest integer)}$$

Correct answer is (118)



PREVIOUS YEARS SOLUTIONS OF JEST

- Q. Electrons of mass m in a thin, long wire at a temperature T follow a one-dimensional Maxwellian velocity distribution. The most probable speed of these electrons is, [JEST 2015]

(a) $\sqrt{\left(\frac{kT}{2\pi m}\right)}$ (b) $\sqrt{\left(\frac{2kT}{m}\right)}$ (c) 0 (d) $\sqrt{\left(\frac{8kT}{\pi m}\right)}$

Soln. The one-dimensional Maxwellian distribution for speed is

$$f(v) = 2 \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv^2}{2k_B T}}; \quad 0 < v < \infty$$

For most probable speed ($v = v_p$), we have

$$\left. \frac{d}{dv} f(v) \right|_{v=v_p} = 0 \Rightarrow v_p = 0.$$

Correct option is (c)

- Q. For which gas the ratio of specific heats (C_p/C_v) will be largest? [JEST 2014]
 (a) mono-atomic (b) di-atomic (c) tri-atomic (d) hexa-atomic

Soln. The ratio of specific heat is

$$\frac{C_p}{C_v} = \frac{\left(\frac{f}{2} + 1\right)R}{\frac{f}{2}R}, \text{ where } f \text{ is the degree of freedom for the gas}$$

$$= 1 + \frac{2}{f}.$$

Since f is minimum for mono-atomic gas, i.e., $f = 3$, C_p/C_v will be largest for mono-atomic gas.

Correct option is (a)

CAREER POINT

Chapter 2

Laws of thermodynamics & their Consequences-1

Laws of Thermodynamics

Zeroth law of thermodynamics :

If two systems are separately in thermal equilibrium with a third system they are also in thermal equilibrium with each other.

This law enables us to compare the temperature of two system with the help of third system. This law can be used to define temperature.

The temperature of a system is the property which determines whether or not a system is in thermal equilibrium with other system.

First law of thermodynamics :

The first law of thermodynamics is simply the principle of conservation of energy applied to the system.

Whenever other forms of energy is converted into heat and viceversa there is a fixed ratio between quantities of energy & heat thus converted.

If an infinitesimal amount of heat dQ is given to the system then its some part is used to do work (dW) and other part is used to change the internal energy (dU)

$$dQ = dU + dW$$

Significance : This law signifies that

- (i) Heat is a form of energy.
 - (ii) Energy is conserved in thermodynamic system.
 - (iii) Every thermodynamic system in equilibrium state possess internal energy which is a function of state only.
- This law signifies the exact relation between heat & other energy. It follows directly from this law that it is impossible to derive any work without expenditure of an equal amount of energy in some other form.

First law of Thermodynamics in different process :

(i) Cyclic Process :

$$dQ = dU + dW$$

For cyclic process $dU = 0$, because internal energy depends only on the state.

$$\int dQ = \int dW$$

ii) Isochoric Process : ($dV = 0$)

$$dQ = dU + dW \quad \text{but} \quad dW = 0, \text{ because } V = \text{constant} \quad dQ = dU$$

If heat is given to the system internal energy increase & if heat is given by the system, internal energy decrease.

iii) Adiabatic Process : ($dQ = 0$)

$$\begin{array}{lll} dQ = dU + dW & \text{or} & Q = \text{constant} \Rightarrow dQ = 0 \\ dU + dW = 0 & \text{or} & dU = -dW = -PdV \end{array}$$

If work is done by the system (in adiabatic process) then internal energy decreases & vice-versa.



iv) Free expansion :

If a system, say, a gas expands in such a way that no heat enters or leaves the system (adiabatic process) and also no work is done by or on the system then the process is called free expansion.

For free expansion $dQ = 0$ and $dW = 0$

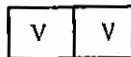
$$\Rightarrow dU = 0 \quad \text{or} \quad U = \text{constant}$$

The initial and final state internal energy are same.

Q. A perfectly insulated box contains a partition dividing the box into two equal parts as shown in the figure.

Initially L.H.S. part contains an ideal monoatomic gas at temperature T and other half is evacuated.

The partition is suddenly removed so that the gas is filled throughout the entire box.



(a) What is the final temperature of the gas

(b) What is the change in internal energy.

(c) What is the work done.

Soln. $dQ = dU + dW$

Since there is no transfer of heat $dQ = 0$

$$P = 0, dW = 0, \Rightarrow dU = 0$$

If internal energy is same, change in temperature is zero $T_1 = T_2$.

Q. Show that $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = 0$

Where α and β are the coefficient of thermal expansion and coefficient of compressibility respectively.

Soln. Since V is a state function so we can write

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right]_T$$

$$\text{or} \quad \left[\frac{\partial}{\partial T}(-V\beta)\right]_P = \left[\frac{\partial}{\partial P}(V\alpha)\right]_T \quad \left[\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\beta, \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha\right]$$

carrying out the differentiation we get

$$-\beta\left(\frac{\partial V}{\partial T}\right)_P - V\left(\frac{\partial \beta}{\partial T}\right)_P = \alpha\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial \alpha}{\partial P}\right)_T$$

$$\text{or} \quad -\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial \beta}{\partial T}\right)_P = \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial \alpha}{\partial P}\right)_T$$

$$\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = -\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\beta}{V}(\alpha V) - \frac{\alpha}{V}(-\beta V) = 0$$

Q. Show that for homogeneous fluid $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$ where the symbols have their usual meaning.

ing.

(a) Hence prove that for a perfect gas

$$C_p - C_v = R$$

(b) Hence prove for a vander Waals' gas

$$C_p - C_v = R(1 + 2a/RTV)$$



Soln. The specific heat at constant pressure and constant volume are given as

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P \quad [dQ = TdS]$$

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

Now if the entropy S is regarded as a function of T and V and since dS is perfect differential $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

$$T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

From Maxwell's 1st relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$

$$\therefore T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

$$\text{Now } C_P - C_V = T \left(\frac{\partial S}{\partial T} \right)_P - T \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad \dots (1)$$

(a) For a perfect gas the equation of state is $PV = RT$ (one mole)

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V} \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = T \left(\frac{R}{V} \right) \left(\frac{R}{P} \right) = \frac{TR^2}{PV} = \frac{R^2 T}{RT} = R$$

(b) For a vander Waals' gas the equation of state is

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (\text{one mole})$$

$$\text{or } \left(P + \frac{a}{V^2} \right) = \frac{RT}{V - b} \quad \dots (2)$$

where a and b are constant

Differentiating eqⁿ (2) w.r.t. T at constant volume we get

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V - b}$$

Differentiating eqⁿ (2) w.r.t. T at constant pressure we get

$$0 - \frac{2a}{V^3} \left(\frac{\partial V}{\partial T} \right)_P = - \frac{RT}{(V - b)^2} \left(\frac{\partial V}{\partial T} \right)_P + \frac{R}{V - b}$$



$$\left(\frac{\partial V}{\partial T}\right)_P \left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right] = \frac{R}{V-b}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right]}$$

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ in equation (1) we have

$$C_P - C_V = T \frac{R}{V-b} \cdot \frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right]} = \frac{R^2 T}{(V-b)^2 \left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right]}$$

$$\text{So } C_P - C_V = \frac{R}{1 - \frac{2a(V-b)^2}{V^3 RT}}$$

Neglecting b in comparison to V ($V \gg b$) $\Rightarrow V-b \sim V$

$$C_P - C_V = \frac{R}{1 - \frac{2a}{V^3} \frac{V^2}{RT}} = \frac{R}{1 - \frac{2a}{RTV}} = R \left(1 - \frac{2a}{RTV} \right)^{-1}$$

Expanding binomially and neglecting higher powers we get

$$C_P - C_V = R \left(1 + \frac{2a}{RTV} \right)$$

Q. From the first law of thermodynamics deduce

$$(i) \quad dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV \quad (ii) \quad C_P = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] V \alpha$$

$$(iii) \quad dQ = C_V dT + \frac{C_P - C_V}{V \beta} dV$$

Soln. Consider a gaseous system whose thermodynamical state is described by any two of three variables (P, V & T)

$$\text{Internal energy } U = f(T, V) \quad \dots (1)$$

According to 1st law of thermodynamics

$$dQ = dU + dW \quad \dots (2)$$

where $dQ \rightarrow$ Amount of heat supplied to the system

$dU \rightarrow$ Change in the internal energy of the system

$dW \rightarrow$ Amount of work done by it.

If the change in the volume of the gas is dV then

$$dW = PdV \quad \dots (3)$$

$$\therefore dQ = dU + PdV \quad \dots (4)$$

Since dU is a perfect differential



$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT \quad \dots (5)$$

Now equation (4) become

$$\begin{aligned} dQ &= \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT + PdV \\ &= \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV \end{aligned} \quad \dots (6)$$

when we are considering the changes in which there is a change in the temperature of the system, the changes at constant temperature would automatically reduce to zero.

Two distinct cases arise.

(i) $V = \text{constant} \Rightarrow dV = 0$

$$\text{Then } dQ = \left(\frac{\partial U}{\partial T} \right)_V dT$$

Heat capacity at constant volume

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Hence eqn (6) becomes

$$dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV \quad \dots (6(a))$$

(ii) Similarly, let $U = f(T, P)$ and $V = f(T, P)$

$$dQ = dU + PdV$$

$$\Rightarrow dQ = \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP + \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT \quad \dots (7)$$

If $U = f(V, P)$ as independent variables

$$dQ = \left(\frac{\partial U}{\partial P} \right)_V dP + \left[\left(\frac{\partial U}{\partial V} \right)_P + P \right] dV \quad \dots (8)$$

When $P = \text{constant} \Rightarrow dP = 0$

So equation (7) become

$$dQ = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT$$

Hence heat capacity at constant pressure

$$C_P = \left(\frac{dQ}{dT} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$\text{But } dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

$$\text{So } \left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V$$



$$C_P = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V + P \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] + \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_P = C_V + \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right]$$

But coefficient of volume expansion is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{So } \left(\frac{\partial V}{\partial T} \right)_P = V\alpha$$

$$\therefore C_P = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] V\alpha \quad \dots (9)$$

(iii) From equation (9)

$$\left(\frac{\partial U}{\partial V} \right)_T + P = \frac{C_P - C_V}{V\alpha}$$

Substituting this value in equation (6(a)) we get

$$dQ = C_V dT + \frac{C_P - C_V}{V\alpha} dV \quad \dots (10)$$

Q. For an ideal gas the molar heat capacity varies as $C = C_V + 3aT^2$. Find the equation of state for the process in the variables T and V where a is constant. C_V is heat capacity at constant volume.

Soln. $dQ = dU + dW \Rightarrow C dT = C_V dT + P dV \Rightarrow (C_V + 3aT^2) dT = C_V dT + P dV$

$$\Rightarrow C_V dT + 3aT^2 dT = C_V dT + P dV \Rightarrow 3aT^2 dT = P dV \Rightarrow 3aT^2 dT = \frac{nRT}{V} dV$$

$$\Rightarrow 3a \int T dT = nR \int \frac{dV}{V} \Rightarrow 3a \frac{T^2}{2} = nR \ln \left(\frac{V}{A} \right) \quad \text{where } A \text{ is a constant of integration.}$$

$$\Rightarrow \frac{3a}{2} \frac{T^2}{nR} = \ln \left(\frac{V}{A} \right) \Rightarrow V = C e^{+3aT^2/2nR}$$

$$\text{or } V e^{-3aT^2/2nR} = \text{constant}$$

for an ideal gas $n = 1$

$$V e^{-3aT^2/2R} = \text{constant}$$

Q. Prove that the fall in temperature by the gas during the adiabatic expansion from pressure P_1 and P_2 at temperature T is given as

$$dT = \frac{T}{C_P} \left(\frac{\partial V}{\partial T} \right)_P dP = \frac{TV\alpha}{C_P} dP$$

Soln. The work done for the adiabatic expansion of a gas is

$$W = PdV \quad \dots (i)$$

From 1st law of thermodynamics $\rightarrow dQ = dU + dW$



For adiabatic change $dQ = 0 \rightarrow dU = -dW = -PdV$

For 1 gm mole of the gas the change in internal energy for a change in temperature by dT is:

$$dU = C_v dT \quad \text{or} \quad dT = \frac{dU}{C_v} = -\frac{PdV}{C_v} \quad \dots (ii)$$

For perfect gas under adiabatic process

$$PV^\gamma = K (\text{constant}) \Rightarrow P^\gamma V^{\gamma-1} dV + V^\gamma dP = 0$$

$$\Rightarrow PdV = -\frac{V^\gamma dP}{\gamma V^{\gamma-1}} = -\frac{V}{\gamma} dP \quad \dots (iii)$$

Now $PV = nRT$ for n mole of gas

$$PdV + VdP = nRdT$$

$$\text{At constant pressure } dP = 0 \Rightarrow P \left(\frac{\partial V}{\partial T} \right)_P = nR$$

$$\text{Hence, } PT \left(\frac{\partial V}{\partial T} \right)_P = nRT \Rightarrow PT \left(\frac{\partial V}{\partial T} \right)_P = PV \quad \text{or} \quad V = T \left(\frac{\partial V}{\partial T} \right)_P$$

Substituting this value of V in equation (iii)

$$\text{We get } PdV = -\frac{T}{\gamma} \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$\text{From equation (ii)} \quad dT = -\frac{PdV}{C_v} = \frac{T}{C_v \gamma} \left(\frac{\partial V}{\partial T} \right)_P dP \quad (\text{using above equation})$$

$$\text{Now } \gamma = \frac{C_p}{C_v}$$

$$\therefore \boxed{dT = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_P dP} \quad \dots (iv)$$

The volume expansion of gas

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Hence

$$\boxed{dT = \frac{TV\alpha}{C_p} dP = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_P dP}$$

Q. If the degree of freedom of a gas is n , then find the ratio of C_p and C_v .

$$\text{Soln. Molar specific heat } C_v = \frac{dU}{dT}, \quad C_v = \frac{d}{dT} \left(\frac{n}{2} RT \right) = \frac{n}{2} R$$

$$C_p - C_v = R, \quad C_p = R + C_v = R + \frac{n}{2} R = \left(1 + \frac{n}{2} \right) R$$

$$\therefore \frac{C_p}{C_v} = \frac{\left(\frac{n}{2} + 1 \right) R}{\frac{n}{2} R} \Rightarrow \boxed{\frac{C_p}{C_v} = 1 + \frac{2}{n}}$$



Q. Gas equation during an adiabatic process : Prove $PV^\gamma = TV^{\gamma-1} = P^{\gamma-1}/T^\gamma = \text{constant}$

Soln. For adiabatic process, $dQ = 0$

$$dU + dW = 0 \Rightarrow nC_v dT + PdV = 0$$

$$\Rightarrow nC_v \frac{dT}{T} + nRT \frac{dV}{V} = 0$$

$$\Rightarrow nC_v \ln T + nR \ln V = 0$$

$$\Rightarrow \frac{nR}{\gamma-1} \ln T + nR \ln V = 0$$

$$\Rightarrow TV^{\gamma-1} = \text{constant}$$

Moreover, we have

$$\frac{PV}{nR} V^{\gamma-1} = \text{constant} \Rightarrow PV^\gamma = \text{constant}$$

Futhermore, we have,

$$P \left(\frac{nRT}{P} \right)^\gamma = \text{constant} \Rightarrow P^{1-\gamma} T^\gamma = \text{constant}$$

Or, $\frac{P^{\gamma-1}}{T^\gamma} = \text{constant}$

Q. When a system is taken from the state A to the state B along the path ACB, 80 joule of heat flows into the system and the system does 30 joule of work.

(i) How much heat flows into the system along the path ADB if work done is 10 J ?

(ii) The system is returned from state B to state A along the curved path. The work done on the system is 20 joule. Does the system absorb or liberate heat and how much?

(iii) If $U_A = 0$, $U_D = 40$ J. Find the heat absorbed in the process AD & DB.

Soln.

(i) $W = 10J$

Heat along ADB

$$dQ = dU + dW = 50 + 10 = 60 \text{ Joule}$$

$$\because dQ = dU + dW$$

$$\Rightarrow dU = 80 - 30 = 50 \text{ Joule}$$

(ii) $dW = -20J$

$$dQ = dU + dW$$

$$= 50 - 20 = 30 \text{ Joule}$$

$$\text{Liberated heat} = 80 - 30 = 50 \text{ Joule}$$

(iii) $U_A = 0$, $U_D = 40J$

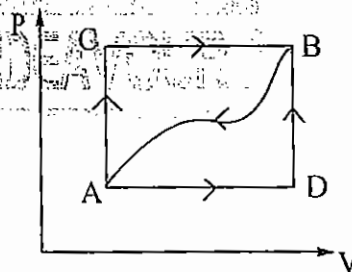
$$\text{for path DB, } \delta W = 0 \Rightarrow dQ = dU$$

$$(U_B - U_A) = 80J$$

$$\text{for path AD, } dU = U_D - U_A = 40J$$

$$dQ = dU + dW = 40 + 10 = 50 \text{ joule}$$

$$\begin{cases} \text{for DB, } dW = 0 \\ \text{for ADB, } dW = 10J \end{cases}$$





Q. A motor car tyre has a pressure of 2 atm at room temperature 27°C . If the tyre suddenly bursts. Find the resulting temperature.

Soln. $P_1 = 2 \text{ atm}$ $P_2 = 1 \text{ atm}$
 $T_1 = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$ $T_2 = ?$
 $\gamma = 1.4$ for air

$$\text{Formula } \frac{P_1^{\gamma-1}}{T_1^\gamma} = \frac{P_2^{\gamma-1}}{T_2^\gamma}$$

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

$$\left(\frac{1}{2}\right)^{1.4-1} = \left(\frac{T_2}{300}\right)^{1.4} \Rightarrow \left(\frac{1}{2}\right)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

$$T_2 = 246.1 \text{ K} = -26.9^\circ\text{C}$$

Q. A quantity of air at 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the i) pressure and ii) temperature.

Soln. Given $P_1 = 1 \text{ atm}$ $P_2 = ?$ $\gamma = 1.4$
 $V_1 = V$ $V_2 = V/2$ $T_1 = 27^\circ\text{C} = 300\text{K}$ $T_2 = ?$
 $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^\gamma = 1 \left(\frac{V}{V/2}\right)^{1.4} = 1(2)^{1.4} = 2.636 \text{ atm}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300 \left(\frac{V}{V/2}\right)^{1.4-1}$$

$$= 300(2)^{0.4} = 395.9\text{K} = 122.9^\circ\text{C}$$

Q. Air is compressed adiabatically of half its volume. Calculate the change in its temperature. Let the initial temperature be T_1 and final temperature T_2

Soln. Initial volume $V_1 = V$ and final volume $V_2 = \frac{V}{2}$

For adiabatic process $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{ or } T_2 = T_1 (2)^{1.4-1}$$

$$T_2 = [2]^{0.4} T_1 = 1.319 T_1$$

So change in temperature.

$$T_2 - T_1 = 1.319 T_1 - T_1 = 0.319 T_1$$



- Q.** 1 gm molecule of a monatomic $\left(\gamma = \frac{5}{3}\right)$ perfect gas at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmosphere. Calculate the resulting difference in temperature.

Soln. Given $P_1 = 1 \text{ atm}$ $P_2 = 50 \text{ atm}$ $T_1 = 27^\circ\text{C} = 300\text{K}$

$$T_2 = ? \quad \gamma = \frac{5}{3}$$

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma-1}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma-1}} \quad \text{or} \quad \left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$(50)^{\frac{5}{3}-1} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}} \Rightarrow 50^{\frac{2}{3}} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}}$$

$$\frac{2}{3} \log 50 = \frac{5}{3} \log T_2 - \frac{5}{3} \log 30$$

$$T_2 = 1434 \text{ K} = 1161^\circ\text{C}$$

Work done during an isothermal process.

- Q.** A certain gas obeys the eqn of state $P(V-b) = RT$
- Derive an expression for heat and work in a reversible isothermal expansion of the gas
 - Derive an expression for heat and work in a reversible adiabatic expansion of the gas
 - Calculate ΔU , Q and W when 1 mol of the gas expands reversibly at 300K from 0.220 to 20.02 litre

(i) isothermally (ii) adiabatically. Assume that $b = 0.020 \text{ lit mol}^{-1}$, $C_V = \frac{3}{2}R$ and $\gamma = \frac{5}{3}$

Soln. (i) $dW = PdV$ or $W = \int_{V_1}^{V_2} PdV$

Given equation of state is $P = \frac{RT}{(V-b)}$

$$\text{Thus } W = \int_{V_1}^{V_2} \frac{RT}{V-b} dV = RT \ln \left(\frac{V_2-b}{V_1-b} \right)$$

$$\begin{aligned} \text{Now, } dU &= \left(\frac{\partial U}{\partial V} \right) dV + \left(\frac{\partial U}{\partial T} \right) dT \quad \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = T \left(\frac{\partial \left(\frac{RT}{V-b} \right)}{\partial T} \right)_V - P \\ &= \frac{RT}{V-b} - P = P - P = 0 \quad \therefore \Delta U = 0 \end{aligned}$$

$$\text{Thus, } \Delta Q = \Delta U - W = -W = RT \ln \left(\frac{V_2-b}{V_1-b} \right)$$



(ii) for adiabatic reversible expansion $\rightarrow Q = 0$

$$\text{Hence } dU = -dW = -\frac{RT}{V-b}dV$$

$$\Rightarrow \int_{T_1}^{T_2} \frac{C_V dT}{T} = - \int_{V_1}^{V_2} \frac{R}{V-b} dV \Rightarrow C_V \ln \left(\frac{T_2}{T_1} \right) = -R \ln \left(\frac{V_2-b}{V_1-b} \right)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_2-b}{V_1-b} \right)^{-R/C_V} = \left(\frac{V_2-b}{V_1-b} \right)^{-(\gamma-1)}$$

$$\therefore W = -\Delta U = -C_V (T_2 - T_1) = -C_V T_1 \left[\left(\frac{V_1-b}{V_2-b} \right)^{\gamma-1} - 1 \right]$$

(iii) $T_1 = T_2 = 300\text{K}$, $V_1 = 0.220$ litre, $V_2 = 20.020$ litre, $b = 0.020$ litre

For isothermal reversible expansion

$$W = -\Delta Q = -RT_1 \ln \left(\frac{V_2-b}{V_1-b} \right) = -(8.314)(300) \ln \left(\frac{20.0}{0.20} \right) = -11.548 \text{ KJ mol}^{-1}$$

$$\Delta U = 0$$

Now, for an adiabatic reversible expansion

$$\Delta Q = 0$$

$$\Delta U = -W = -C_V T_1 \left[\left(\frac{V_1-b}{V_2-b} \right)^{\gamma-1} - 1 \right]$$

Given $C_V = \frac{3}{2}R$, $\gamma = \frac{5}{3}$ and $T_1 = 300\text{K}$

$$\Delta U = -W = -\left(\frac{3}{2}R \right) (300) \left[\left(\frac{200}{20000} \right)^{2/3} - 1 \right] = 3.554 \text{ kJ.}$$

Slope of Adiabatic and Isothermal Process

(a) **Isothermal Process** : For an ideal gas, we have

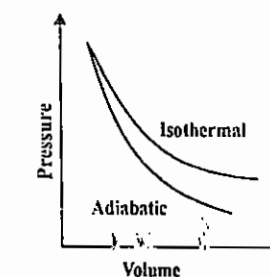
$$PV = \text{constant} \Rightarrow PdV + VdP = 0 \Rightarrow \left(\frac{dP}{dV} \right)_{\text{iso}} = -\frac{P}{V}$$

(b) **Adiabatic Process** : For an ideal gas, we have

$$PV^\gamma = \text{Constant} \Rightarrow P\gamma V^{\gamma-1}dV + dP \cdot V^\gamma = 0 \Rightarrow \frac{dP}{dV} = -\frac{PV^{\gamma-1}\gamma}{V^\gamma}$$

$$\Rightarrow \left(\frac{dP}{dV} \right)_{\text{adia}} = -\gamma \frac{P}{V}$$

$$\therefore \frac{\left(\frac{dP}{dV} \right)_{\text{adia}}}{\left(\frac{dP}{dV} \right)_{\text{iso}}} = \gamma > 1$$

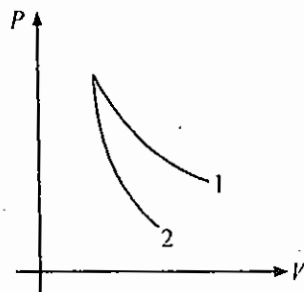


... (35)

This shows that slope of adiabatic is γ -times than that of isothermal. Moreover, the adiabatic constant (γ) can also be defined as the ratio of slope of P - V curve for an adiabatic process to slope of P - V curve for an isothermal process.



- Q. P - V plots for two gases during adiabatic processes are shown in the figure. Plots 1 and 2 should correspond respectively to



- (a) He and O_2 (b) O_2 and He (c) He and Ar (d) O_2 and N_2

Soln. In adiabatic process, $PV^\gamma = \text{constant}$

Therefore, slope of P - V graph, $\frac{dP}{dV} = -\gamma \frac{P}{V}$

$$\Rightarrow \text{slope} \propto \gamma \quad (\text{with negative sign})$$

From the given graph, $(\text{slope})_2 > (\text{slope})_1$

$$\therefore \gamma_2 > \gamma_1$$

Therefore, 1 should correspond to O_2 ($\gamma = 1.4$) and 2 should correspond to He ($\gamma = 1.67$).

Correct option is (b)

- Q. If the eqn of state for a gas with internal energy U is $PV = \frac{1}{3}U$ then the equation for an adiabatic process is:

(i) $PV^{1/3} = \text{constant}$

(ii) $PV^{2/3} = \text{constant}$

(iii) $PV^{4/3} = \text{constant}$

(iv) $PV^{3/5} = \text{constant}$

Soln. For adiabatic process

$$dQ = 0$$

$$dU = -dW = -PdV$$

But $PV = \frac{1}{3}U \rightarrow U = 3PV$

$$d(3PV) = -PdV = 3PdV + 3VdP = -PdV$$

$$3VdP = -4PdV \quad \text{or} \quad \frac{dP}{P} = -\frac{4}{3} \frac{dV}{V}$$

Integrating, $\log P = -\frac{4}{3} \log V + \log C$

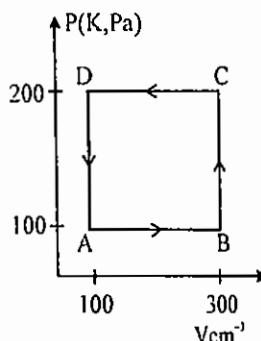
$\log P + \log V^{4/3} = \log C \Rightarrow \log PV^{4/3} = \log C$ here C is a constant

$$PV^{4/3} = \text{constant}$$

Option (iii) is correct



- Q. A thermodynamic system is taken through the cycle ABCDA as shown in figure. (i) Calculate the work done by the gas (system) during the path AB, BC, CD, DA. (ii) Find the total heat rejected by the gas during the process ABCDA.



Soln. (i) $W_1 = P\Delta V = 100 \text{ KPa} \times 200 \text{ cm}^3$ (along AB)

$$= 100 \times 1000 \times \frac{200 \text{ Pa}}{10^6 \text{ m}^3} = 20 \text{ J}$$

$W_2 = 0$ because the change in volume = 0 (along BC)

$$W_3 = P \times \Delta V = -200 \text{ KPa} \times 200 \text{ cm}^3 = -200 \times 1000 \times \frac{200 \text{ Pa}}{10^6 \text{ m}^3} = -40 \text{ J} \quad (\text{along CD})$$

The negative sign is due to decrease in volume

$W_4 = 0$ (along DA)

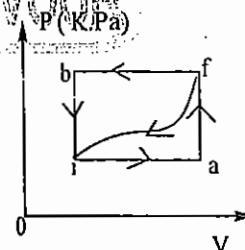
$$\therefore W = W_1 + W_2 + W_3 + W_4 = 20 - 40 = -20 \text{ J}$$

(ii) $dQ = dU + dW$

For cyclic process, $dU = 0$

$$dQ = dW = -20 \text{ J} \rightarrow \text{Heat rejected by the gas.}$$

- Q. When a system is taken from a state i to f along the path i a f as shown in figure. It is found that heat Q absorbed by the system is 50 cal and the work done by the system is 20 cal. Along the path i b f $Q = 36 \text{ cal}$
- (i) What is the work done along the path i b f?



- (ii) If the work done on the system is equal to 13 cal for the curved returned path fi. What is the value Q for this path?
- (iii) If U of the system in initial state is equal to 10 cal. What is the internal energy of the system in final state?
- (iv) If internal energy of the system for state B = 22 cal. What are the values Q for the process b f and i b?

Soln. Given: $U_i = 10 \text{ cal}$, $Q = 50 \text{ cal}$, and $W = 20 \text{ cal}$ for the path i a f

$$(i) \quad Q = U_f - U_i + W \Rightarrow 50 = U_f - 10 + 20$$

$$\Rightarrow \boxed{U_f = 40 \text{ cal}}$$



So work done along ibf

as $dQ = 36$

$$dQ = dU + dW$$

$$\Rightarrow dW = dQ - dU = 36 - (40 - 10) = \boxed{6 \text{ cal}}$$

(ii) $W = 13 \text{ cal}$ for (of \rightarrow i), $W = -13 \text{ cal}$, $dQ = dU + dW$
 $= (U_i - U_f) - 13 = -30 - 13 = -43 \text{ Cal}$

(iii) $\Delta U = 30$

$$\Rightarrow U_f - U_i = 30 \quad \Rightarrow U_f - 10 = 30 \Rightarrow \boxed{U_f = 40}$$

(iv) $U_b = 22 \text{ cal}$ $U_i = 10 \text{ cal}$

So for path b f $\Rightarrow U_f - U_i = 18 \text{ cal}$

$$\Rightarrow \text{for } b \rightarrow \Delta W = 0$$

so $dQ = dU$

$$\Rightarrow \boxed{dQ = 18 \text{ cal}}$$

For path i \rightarrow b

$$\Delta U = U_b - U_i = 12$$

$$dQ = \Delta U + dW$$

As $\Delta W = 6$ {because for $b \rightarrow f$ $\Delta W = 0$ }

$$dQ = 12 + 6 = 18 \text{ cal}$$

$$\Rightarrow \boxed{dQ = 18 \text{ cal}}$$

Q. An ideal gas expands adiabatically but quasistatically from state i (P_i, V_i, T_i) to a state f (P_f, V_f, T_f). What is the change in its internal energy? What would this change be if the expansion were isothermal?

Soln. **Quasistatic process :** If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium, the process is called quasistatic this means we can specify pressure, volume, temperature uniquely at any instant during such a process. Thus a quasistatic process is an idealised process in which all changes take place infinitely slowly from 1st law $dQ = dU + dW$

But for adiabatic process $dQ = 0$

So $dU = -dW$

$$\text{Total change in internal energy} = \int_i^f dU = - \int_i^f P dV = - \int_i^f \frac{K}{V^\gamma} dV$$

$$\text{So } U_f - U_i = -K \left(\frac{V^{-\gamma+1}}{-\gamma+1} \right)_i^f \quad \left\{ \begin{array}{l} \text{as } PV^\gamma = K \\ P = \frac{K}{V^\gamma} \end{array} \right.$$

$$= \frac{K}{1-\gamma} (V^{-\gamma+1})_i^f$$

But $P_i V_i^\gamma = P_f V_f^\gamma = K$

$$\text{So } U_f - U_i = \frac{1}{1-\gamma} (P_f V_f^\gamma V_f^{-\gamma+1} - P_i V_i^\gamma V_i^{-\gamma+1})$$

$$= \frac{1}{1-\gamma} (P_f V_f - P_i V_i) \quad \text{use } PV = RT$$

$$\boxed{\Delta U = \frac{R}{1-\gamma} (T_f - T_i)}$$



(ii) for isothermal expansion $T_i = T_f$

$$U_f - U_i = \frac{R}{1-\gamma} (T_f - T_i) = 0$$

So for quasistatic isothermal process, the change in internal energy is Zero.

Q. Figure shows a process ABCA performed on an ideal gas. Find the net heat given to the system during the process.

Soln. Since the process is cyclic so the change in internal energy $dU = 0$

$$\text{Since } dU = 0 \Rightarrow dQ = dW = PdV$$

For the process AB change in volume = Zero

$$\Rightarrow W_1 = 0$$

For process BC \rightarrow Temp is constant

$$W_2 = \int_{V_1}^{V_2} dW_2 = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{TR}{V} dV$$

$$W_2 = RT \ln V \Big|_{V_1}^{V_2} = RT_2 \ln \frac{V_2}{V_1}$$

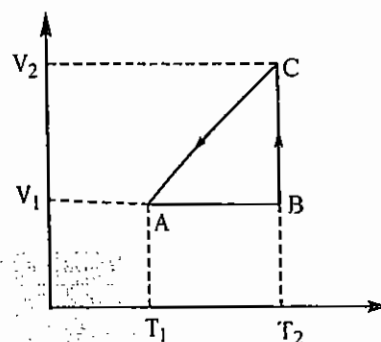
For process AC $\rightarrow \frac{V}{T} = \text{constant}$

$$PV = RT \Rightarrow \frac{V}{T} = \frac{R}{P} \Rightarrow V = \frac{RT}{P} \Rightarrow dV = \frac{R}{P} dT$$

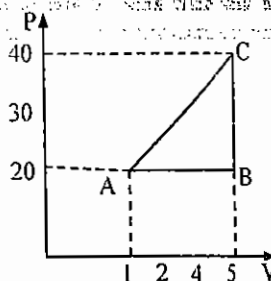
$$W_3 = \int_{T_2}^{T_1} dW = \int_{T_2}^{T_1} PdV = \int_{T_2}^{T_1} P \frac{R}{P} dT = [RT]_{T_2}^{T_1} = R(T_1 - T_2)$$

$$W_3 = R(T_1 - T_2)$$

$$\text{Now } Q = W = W_1 + W_2 + W_3 = R \left[T_2 \ln \frac{V_2}{V_1} + (T_1 - T_2) \right]$$



Q. A gas is carried through a cycle ABCA as shown in the P-V diagram fig. Determine whether the heat is given to the system or by the system. Work done by the system or on the system. Internal energy of the system increases or decreases in the following process.



(i) For the process AB if $\Delta U = +Ve$

(ii) For the process BC if $Q = +Ve$

(iii) For process CA

(iv) For AB net work done in the complete cycle.

Soln. (i) $\Delta U = +Ve$ (given) \rightarrow so internal energy of the system increase

$\Delta W = +Ve$ (work done by the system because volume increase)

$\Delta Q = \Delta U + \Delta W = +Ve$ (Heat given to the system)

(ii) For BC

$Q = +Ve$ (given) \rightarrow Heat given to the system



$\Delta W = 0$ (because $V = \text{Const}$ $W = PV$, $dV = 0$, So $W = 0$)

$\Delta U = +Ve$ $\Delta Q = \Delta U + \Delta W$. Internal energy of the system increase)

(iii) For process CA

For process ABC $\Delta U = +Ve$ ($\because (\Delta U)_{AC} = (\Delta U)_{AB} + (\Delta U)_{BC} = +Ve + +Ve$)

For CA Process $(\Delta U)_{CA} = -(\Delta U)_{AC} = -Ve$

$(\Delta U)_{CA} = -ve$ (Internal energy of the system decrease)

$\Delta W = -ve$ (\because volume decrease so workdone on the system)

$\Delta Q = -ve$ ($\Delta Q = \Delta U + \Delta W = -ve$, heat is given by the system)

(iv) Net workdone in couple cycle = area under the curve

$$= \frac{1}{2} \times AB \times BC = \frac{1}{2} \times 3 \times 20 = 30 \text{ Joule.}$$

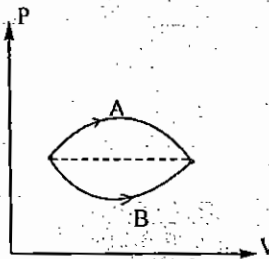
Q. Fig shows the process A and B on a system. Let ΔQ_1 and ΔQ_2 be the heat given to the system in the process A and B respectively. Then,

(i) $\Delta Q_1 > \Delta Q_2$

(ii) $\Delta Q_1 = \Delta Q_2$

(iii) ΔW

(iv) $\Delta Q_1 \leq \Delta Q_2$



Soln. Since ΔU is same for both the process and ΔW is the amount of work which is represented by the area under the curve.

$$\Delta Q = \Delta U + \Delta W \rightarrow \Delta Q \text{ will vary as } \Delta W$$

Since area under A is greater than area under B

$$\Rightarrow \Delta W_A > W_B, \text{ so } \Delta Q_1 > \Delta Q_2$$

if both the arrow signs are changed then

$$\Delta Q_1 < \Delta Q_2$$

Q. P, V and T for a certain gas are related by $P = \frac{\alpha T - \beta T^2}{V}$, where α and β are constants. Find the workdone by the gas if the temperature changes from T_1 to T_2 while pressure remains constant.

Soln. $PV = RT \Rightarrow PdV = RdT$,

(\because Pressure is constant)

$$\Rightarrow dV = \frac{RdT}{P}$$

$$\text{So, } dW = PdV = \alpha T - \beta T^2 \Rightarrow dW = \alpha dT - 2\beta TdT,$$

$$\Rightarrow W = \alpha \int_{T_1}^{T_2} dT - 2\beta \int_{T_1}^{T_2} TdT \Rightarrow W = \alpha(T_2 - T_1) - \beta(T_2^2 - T_1^2).$$



Reversible and Irreversible processes

Reversible Process : A reversible process is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in the opposite order and sense and no changes are left in any of the bodies taking part in the process or in the surrounding.

The condition for reversibility :

A process can be reversible only when it satisfy two condition.

- (i) Process must be quasistatic (If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium)

A quasistatic process is an idealised process in which all changes take place infinitely slowly.

- (ii) Process must be non-dissipative (dissipative force such as friction, resistance, Hysteresis etc must be completely absent).

Q. Classify the reversible & irreversible process among the following:

- Soln.** (1) Isothermal expansion of a gas → irreversible
 (2) Isothermal quasistatic expansion of a gas → Reversible
 (3) Adiabatic expansion of a gas → Irreversible
 (4) Diffusion of a gas → irreversible
 (5) Transfer of heat from hot body to cold body → irreversible
 (6) Free expansion of a perfect gas → irreversible
 (7) Transfer of heat by radiation → irreversible
 (8) Electrical heating of wire → irreversible
 (9) Very slow expansion or contraction of a spring → Reversible

Q. An ideal gas expands in a process in which its pressure depends on the volume as $p = p_0 e^{-\alpha V}$, where p_0 and α are two positive constants. If n is the number of moles in the gas, the maximum temperature that it will attain in this process is (R is the universal gas constant)

- (a) $p_0 / e \alpha n R$ (b) $p_0 / \alpha n^3 R$ (c) $e p_0 / \alpha n R$ (d) $p_0^2 / \alpha n R$

Soln. For an ideal gas, we have

$$PV = nRT \text{ or } T = \frac{PV}{nR} = \frac{P_0 V}{nR} e^{-\alpha V}$$

For temperature to be maximum, we have

$$\frac{dT}{dV} = 0$$

$$\Rightarrow \frac{P_0 V}{nR} (-\alpha) e^{-\alpha V} + \frac{P_0}{nR} e^{-\alpha V} = 0$$

$$\Rightarrow 1 - V\alpha = 0 \quad \Rightarrow \quad V\alpha = 1$$

$$\Rightarrow \quad V = \frac{1}{\alpha}$$

$$\therefore T_{\max} = \frac{P_0}{nR} \cdot \frac{1}{\alpha} e^{-\alpha \cdot \frac{1}{\alpha}} = \frac{P_0}{e \alpha n R}$$

Correct option is (a)



PREVIOUS YEARS SOLUTIONS OF TIFR

- Q. In the temperature range $100 - 1000^\circ\text{C}$, the molar specific heat of a metal varies with temperature T (measured in degrees Celsius) according to the formula $C_p = (1 + T/5) \text{ J-deg } ^\circ\text{C}^{-1} \text{ mol}^{-1}$. If 0.2 kg of the metal at 600°C is brought in thermal contact with 0.1 kg of the same metal at 300°C , the final equilibrium temperature, in deg C, will be

[Assume that no heat is lost due to radiation and/or other effects].

[TIFR 2016]

- (a) 466 (b) 567 (c) 383 (d) 519

Soln.

$M_1 = 0.2 \text{ kg}$	$M_2 = 0.1 \text{ kg}$
$T_1 = 600^\circ\text{C}$	$T_2 = 300^\circ\text{C}$
$= 873 \text{ K}$	$= 573 \text{ K}$

Using the principle of calorimetry

Heat loss = Heat gain

$$\text{We have, } -\left(\int dQ\right)_{\text{loss}} = \left(\int dQ\right)_{\text{gain}} \Rightarrow -\int_{T_1}^{T_f} M_1 C_p dT = \int_{T_2}^{T_f} M_2 C_p dT$$

where T_f is the final equilibrium temperature.

$$\Rightarrow -0.2 \int_{T_1}^{T_f} \left(1 + \frac{T}{5}\right) dT = 0.1 \int_{T_2}^{T_f} \left(1 + \frac{T}{5}\right) dT$$

$$\Rightarrow -2 \left[T + \frac{T^2}{10} \right]_{873}^{T_f} = \left[T + \frac{T^2}{10} \right]_{573}^{T_f}$$

$$\Rightarrow -2 \left(T_f + \frac{T_f^2}{10} \right) + 2 \left(873 + \frac{873^2}{10} \right) = \left(T_f + \frac{T_f^2}{10} \right) - \left(573 + \frac{573^2}{10} \right)$$

$$\Rightarrow 3 \left(T_f + \frac{T_f^2}{10} \right) = 2 \left(873 + \frac{873^2}{10} \right) - \left(573 + \frac{573^2}{10} \right)$$

$$\Rightarrow T_f^2 + 10 T_f - 625259 = 0$$

$$\Rightarrow T_f = \frac{-10 \pm \sqrt{10^2 + 4 \times 625259}}{2} = 785.7 \text{ K}, -795.7 \text{ K (not admirable)}$$

So, $T_f = 785.7 \text{ K} = 512.7^\circ\text{C}$.

The nearest answer is (d).

Correct option is (d)

- Q. A monatomic gas is described by the equation of state $p(V - bn) = nRT$ where b and R are constants and other quantities have their usual meanings. The maximum density (in moles per unit volume) to which this gas can be compressed is

[TIFR 2013]

- (a) $\frac{1}{bn}$ (b) b (c) $\frac{1}{b}$ (d) infinity

Soln. Given : $p(V - bn) = nRT$



$$\Rightarrow \frac{nRT}{V} = p \left(1 - \frac{bn}{V} \right)$$

Taking $\frac{n}{V} = \rho$ (the density), we have

$$RT\rho = p(1 - b\rho) \text{ or } \rho = \frac{p}{pb + RT}$$

For maximum density, we have $\frac{d\rho}{dp} = 0$

$$\frac{(pb + RT) - pb}{(pb + RT)^2} = 0 \Rightarrow T = 0$$

$$\text{Therefore, } \rho_{\max} = \rho|_{T=0} = \frac{p}{pb} = \frac{1}{b}$$

Correct option is (c)

- Q. An ideal diatomic gas is initially at a temperature $T = 0^\circ\text{C}$. Then it expands reversibly and adiabatically to 5 times its volume. Its final temperature will be approximately [TIFR 2015]
 (a) -180°C (b) -150°C (c) -130°C (d) 0°C

Soln. For adiabatic process of ideal gas, we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \text{ where } T_1 = 273 \text{ K}, V_2 = 5V_1, \gamma = \frac{7}{5} \text{ (for diatomic gas)}$$

$$\text{Therefore, } T_2 = 273 \left(\frac{V_1}{5V_1} \right)^{\frac{7}{5}-1} = \frac{273}{5^{2/5}} = 143.4 \text{ K} = -129.59^\circ\text{C} \approx -130^\circ\text{C}$$

Correct option is (c)

- Q. A car tyre is slowly pumped up to a pressure of 2 atmospheres in an environment at 15°C . At this point, it bursts. Assuming the sudden expansion of the air (a mixture of O_2 and N_2) that was inside the tyre to be adiabatic, its temperature after the burst is [TIFR 2010]
 (a) -55°C (b) -37°C (c) -26°C (d) $+9^\circ\text{C}$

Soln. For adiabatic expansion, we have

$$P^{1-\gamma} T^\gamma = \text{constant or } T P^{(1-\gamma)/\gamma} = \text{constant or } T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}, \text{ where}$$

$$T_1 = 288 \text{ K} ; P_1 = 2 \text{ atm}$$

$$T_2 = ? ; P_2 = 1 \text{ atm}$$

$$\Rightarrow T_2 = 288 \left(\frac{2}{1} \right)^{(1-\gamma)/\gamma}, \text{ where } \gamma = 1.4 \text{ (for air).}$$

$$\therefore T_2 = 288 (2)^{-2/7} = 236.25 \text{ K} = -36.7^\circ\text{C}$$

Correct option is (b)

- Q. A thermally-insulated container of volume V_0 is divided into two equal halves by a non-permeable partition. A real gas with equation of state. [TIFR 2014]

$$b^3 \left(p + \frac{a^2}{V^3} \right) = nRT$$



where 'a' and 'b' are constants, is confined to one of these halves at a temperature T_0 . The partition is now removed suddenly and the gas is allowed to expand to fill the entire container. The final temperature of the gas, in terms of its specific heat C_v , will be

- (a) $T_0 - \frac{3a^2}{2C_v V_0^2}$ (b) $T_0 - \frac{2a^2}{3C_v V_0^2}$ (c) $T_0 + \frac{3a^2}{2C_v V_0^2}$ (d) $T_0 + \frac{2a^2}{3C_v V_0^2}$

Soln. For free expansion, we have $dU = 0$, where $U = U(T, V)$.

$$\text{So, } \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = 0, \text{ where } \left(\frac{\partial U}{\partial T} \right)_V = C_v$$

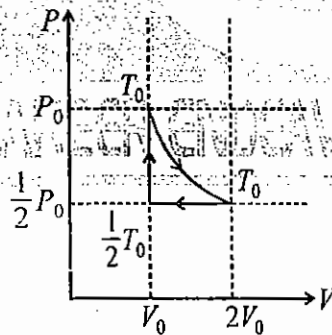
$$\text{and } \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = T \left(\frac{nR}{b^3} \right) - \left(\frac{nRT}{b^3} - \frac{a^2}{V^3} \right) = \frac{a^2}{V^3}$$

$$\begin{aligned} \therefore C_v dT + \frac{a^2}{V^3} dV &= 0 & \Rightarrow C_v \int_{T_0}^{T_f} dT + a^2 \int_{V_0}^{V_0/2} dV &= 0 \\ \Rightarrow C_v (T_f - T_0) + \frac{3a^2}{2V_0^2} &= 0 & \Rightarrow T_f = T_0 - \frac{3a^2}{2C_v V_0^2} \end{aligned}$$

Correct option is (a)

Q. One mole of monoatomic ideal gas is initially at pressure P_0 and volume V_0 . The gas then undergoes a three-stage cycle consisting of the following processes: [TIFR 2017]

- (i) An isothermal expansion till it reaches volume $2V_0$, and heat Q flows into the gas
- (ii) An isobaric compression back to the original volume V_0
- (iii) An isochoric increase in pressure till the original pressure P_0 is regained



The corresponding P-V diagram is shown above

The efficiency of this cycle can be expressed as

- (a) $\epsilon = \frac{4Q + 2RT_0}{4Q + RT_0}$ (b) $\epsilon = \frac{4Q + 2RT_0}{4Q - 3RT_0}$ (c) $\epsilon = \frac{4Q - 2RT_0}{4Q + RT_0}$ (d) $\epsilon = \frac{4Q - 2RT_0}{4Q + 3RT_0}$

Soln. (i) For isothermal process,

The amount of work done is $W_1 = Q$.

This is positive as the gas is expanding in this process.

(ii) For isobaric process,

The amount of work done is

$$W_2 = \frac{P_0}{2} (V_0 - 2V_0) = -\frac{P_0 V_0}{2} = -\frac{RT_0}{2},$$



and the amount of heat exchanged is

$$\Delta Q_2 = nC_p \Delta T = \frac{5}{2}R \left(\frac{T_0}{2} - T_0 \right) = -\frac{5RT_0}{4}.$$

Since $\Delta Q_2 < 0$, this amount of heat flows out of the system.

(iii) For isochoric process,

The amount of work done is $W_3 = 0$, and the amount of heat exchanged is

$$\Delta Q_3 = nC_v \Delta T = \frac{3}{2}R \left(T_0 - \frac{T_0}{2} \right) = \frac{3RT_0}{4}.$$

This amount of heat ΔQ_3 being positive enters into the system.

Therefore, $\eta = \frac{\text{Total work done}}{\text{Heat input}}$

$$= \frac{Q - \frac{RT_0}{2}}{Q + \frac{3RT_0}{4}} = \frac{4Q - 2RT_0}{4Q + 3RT_0}.$$

Correct option is (d)

Q. A thermally isolated container stores N_2 gas at 27.24°C at one atmospheric pressure. Suddenly the pressure of the gas is increased to two atmospheric pressures. Assuming N_2 to behave as an ideal gas, estimate the change in temperature of the gas, in Celsius degree ($^\circ\text{C}$). [TIFR 2017]

Soln. Since the pressure of the gas is suddenly increased, the process must be adiabatic. Hence, we have

$$\begin{aligned} P_1^{1-\gamma} T_1^\gamma &= P_2^{1-\gamma} T_2^\gamma \\ \Rightarrow T_2 &= \left(\frac{P_1}{P_2} \right)^{1-\gamma/\gamma} T_1, \text{ where } \gamma = \frac{7}{5} \text{ for } N_2 \text{ gas} \\ \therefore T_2 &= \left(\frac{1}{2} \right)^{-2/7} \times 300.24 \approx 366 \text{ K} = 93^\circ\text{C}. \end{aligned}$$

Therefore, change in temperature = $93.00 - 27.24$

$$= 65.76$$

$$\approx 66^\circ\text{C}$$

Correct answer is (66)

PREVIOUS YEARS SOLUTIONS OF JEST

Q. A metal bullet comes to rest after hitting its target with a velocity of 80 m/s . If 50% of the heat generated remains in the bullet, what is the increase in its temperature? (The specific heat of the bullet = $160 \text{ Joule per Kg per degree. C}$) [JEST 2013]

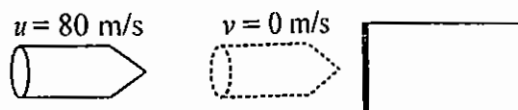
- (a) 14°C (b) 12.5°C (c) 10°C (d) 8.2°C

Soln. If u and v be the final velocity of the bullet then, the change in the bullet's energy is

$$\Delta K = \frac{1}{2}m(v)^2 - \frac{1}{2}m(u)^2 = -\frac{m}{2}(80)^2,$$



where m is the mass of the bullet.



If 50% of this energy remains in the bullet in the form of heat, then

$$50\% \text{ of } \frac{m}{2} (80)^2 = ms\Delta T$$

where ' s ' is the specific heat of the bullet.

$$\begin{aligned} \text{Therefore, } \Delta T &= \frac{1}{4} \times \frac{(80)^2}{160} \quad [\because s = 160 \text{ J kg}^{-1} \text{ } ^\circ\text{C}^{-1}] \\ &= 10^\circ\text{C.} \end{aligned}$$

Correct option is (a)

- Q. In a thermodynamic process, the volume of one mole of an ideal is varied as $V = aT^{-1}$, where a is a constant. The adiabatic exponent of the gas is γ . What is the amount of heat received by the gas if the temperature of the gas increases ΔT in the process? [JEST 2018]

- (a) $R\Delta T$ (b) $\frac{R\Delta T}{1-\gamma}$ (c) $\frac{R\Delta T}{2-\gamma}$ (d) $R\Delta T \frac{2-\gamma}{\gamma-1}$

Soln. Given : $V = aT^{-1} = \frac{a}{T}$

From first law of thermodynamics,

$$dQ = dU + PdV \quad \text{where, } dU = \frac{f}{2} nRdT \quad (\text{for an ideal gas})$$

$$\begin{aligned} \therefore dQ &= \frac{f}{2} nRdT + \frac{nRT}{V} dV \\ &= \frac{f}{2} nRdT + \frac{nRT}{a/T^2} \left(\frac{-a}{T^2} \right) dT = \frac{f}{2} nRdT - nRdT = \left(\frac{f}{2} - 1 \right) nRdT \end{aligned}$$

For 1 mole,

$$dQ = \left(\frac{f}{2} - 1 \right) RdT$$

$$\therefore \Delta Q = \left(\frac{f}{2} - 1 \right) R\Delta T \quad \text{where, } \gamma = 1 + \frac{2}{f} \text{ or } \frac{f}{2} = \frac{1}{\gamma-1}$$

$$\therefore \Delta Q = \left(\frac{1}{\gamma-1} - 1 \right) R\Delta T = R\Delta T \left(\frac{2-\gamma}{\gamma-1} \right)$$

Correct option is (d)

- Q. For a diatomic ideal gas near room temperature, what fraction of the heat supplied is available for external work if the gas is expanded at constant pressure? [JEST 2013]

- (a) $1/7$ (b) $5/7$ (c) $3/4$ (d) $2/7$

Soln. From first law of thermodynamics, $dQ = dU + PdV$.

$$\text{Therefore, } \frac{dW}{dQ} = \frac{PdV}{dU + PdV} = \frac{nRdT}{\frac{f}{2} nRdT + nRdT} = \frac{2}{f+2}.$$



where $PdV = nR dT$ (at constant pressure), and $f = 5$ (for diatomic gas).

Therefore, $\frac{dW}{dQ} = \frac{2}{7}$.

Correct option is (d)

- Q.** A monoatomic ideal gas at 17°C is adiabatically compressed to $1/8$ of its original volume. The temperature after compression is [JEST 2012]

- (a) 2.1°C (b) 17°C (c) -200.5°C (d) 887°C

Soln. For adiabatic process, we have

$$TV^{\gamma-1} = \text{constant.}$$

$$\text{So, } T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}, \text{ where } T_1 = 17^\circ\text{C} = 290 \text{ K, } V_2 = \frac{1}{8} V_1, \gamma = \frac{5}{3} \text{ (for monatomic gases)}$$

$$\text{Therefore, } T_2 = 290 \left(\frac{V_1}{V_1/8} \right)^{2/3} = 290(2)^2 = 1160 \text{ K} = 887^\circ\text{C.}$$

Correct option is (d)

- Q.** After the detonation of an atom bomb, the spherical ball of gas was found to be 15 meter radius at a temperature of $3 \times 10^5 \text{ K}$. Given the adiabatic expansion coefficient $\gamma = \frac{5}{3}$, what will be the radius of the ball when its temperature reduces to $3 \times 10^3 \text{ K}$? [JEST 2017]

- (a) 156 m (b) 50 m (c) 150 m (d) 100 m

Soln. For adiabatic process, we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\text{where } V = \frac{4}{3} \pi r^3$$

$$\therefore T_1 r_1^{3(\gamma-1)} = T_2 r_2^{3(\gamma-1)}$$

$$\Rightarrow r_2 = \left(\frac{T_1}{T_2} \right)^{1/3(\gamma-1)} r_1$$

$$\Rightarrow r_2 = \left(\frac{3 \times 10^5}{3 \times 10^3} \right)^{1/3} \times 15 = 150 \text{ m.}$$

Correct option is (c)

- Q.** An ideal gas is compressed adiabatically from an initial volume V to a final volume αV and a work W is done on the system in doing so. The final pressure of the gas will be $\left(\gamma = \frac{C_p}{C_v} \right)$, [JEST 2015]

- (a) $\frac{W}{V^\gamma} \frac{1-\gamma}{\alpha-\alpha^\gamma}$ (b) $\frac{W}{V^\gamma} \frac{\gamma-1}{\alpha-\alpha^\gamma}$ (c) $\frac{W}{V} \frac{1-\gamma}{\alpha-\alpha^\gamma}$ (d) $\frac{W}{V} \frac{\gamma-1}{\alpha-\alpha^\gamma}$

Soln. For adiabatic process, $P_1 V_1^\gamma = P_2 V_2^\gamma$, where $V_1 = V$ and $V_2 = \alpha V$.



Therefore, $P_1 V_1^\gamma = P_2 (\alpha V)^\gamma \Rightarrow P_1 = P_2 \alpha^\gamma$

Also, the work done for an adiabatic process is

$$\text{Work} = \frac{1}{\gamma-1} (P_1 V_1 - P_2 V_2)$$

$$\Rightarrow -W = \frac{1}{\gamma-1} (P_2 \alpha^\gamma V - P_2 \alpha V)$$

$$\Rightarrow P_2 = -\frac{W(\gamma-1)}{(\alpha^\gamma - \alpha)V} = \frac{W}{V} \frac{\gamma-1}{\alpha - \alpha^\gamma}$$

Correct option is (d)

Q. A theoretical model for a real (non-ideal) gas gives the following expressions for the internal energy (U) and the

pressure (P), $U(T, V) = aV^{-2/3} + bV^{2/3}T^2$ and $P(T, V) = \frac{2}{3}aV^{-5/3} + \frac{2}{3}bV^{-1/3}T^2$, where a and b are con-

stants. Let V_0 and T_0 be the initial volume and initial temperature respectively. If the gas expands adiabatically, the volume of the gas is proportional to [JEST 2018]

- (a) T (b) $T^{3/2}$ (c) $T^{-3/2}$ (d) T^{-2}

Soln. Given: $U(T, V) = aV^{-2/3} + bV^{2/3}T^2$ and $P(T, V) = \frac{2}{3}aV^{-5/3} + \frac{2}{3}bV^{-1/3}T^2$

For adiabatic process, $dU + PdV = 0$

$$\Rightarrow -\frac{2}{3}aV^{-5/3}dV + \frac{2}{3}bV^{-1/3}T^2dV + 2bV^{2/3}TdT + \frac{2}{3}aV^{-5/3}dV + \frac{2}{3}bV^{-1/3}T^2dV = 0$$

$$\Rightarrow \frac{4}{3}bV^{-1/3}T^2dV + 2bV^{2/3}TdT = 0$$

$$\Rightarrow \frac{2}{3}V^{-1}dV + \frac{dT}{T} = 0$$

Integrating, we have

$$\frac{2}{3} \ln V + \ln T = \text{constant}$$

$$\Rightarrow VT^{3/2} = \text{constant} \Rightarrow V \propto T^{-2/3}$$

Correct option is (c)

Q. An ideal gas has a specific heat ratio $C_p/C_v = 2$. Starting at a temperature T_1 the gas under goes an isothermal compression to increase its density by a factor of two. After this an adiabatic compression increases its pressure by a factor of two. The temperature of the gas at the end of the second process would be:

- (a) $\frac{T_1}{2}$ (b) $\sqrt{2}T_1$ (c) $2T_1$ (d) $\frac{T_1}{\sqrt{2}}$ [JEST 2016]

Soln. Since $\frac{C_p}{C_v} = 2$, so $\gamma = 2$

For isothermal process,

$$PV = \text{constant, where density, } \rho = \frac{n}{V}$$



So, $\frac{P}{\rho} = \text{constant}.$

Therefore, the pressure also gets doubled when the density gets doubled.

Now, for an adiabatic process, $T_1 P_1^{\frac{1}{\gamma}-1} = T_2 P_2^{\frac{1}{\gamma}-1}$, where $P_1 = 2P$ and $P_2 = 2P_1 = 4P$.

Therefore, $T_1 (2P)^{-1/2} = T_2 (4P)^{-1/2} \quad [\because \gamma = 2]$

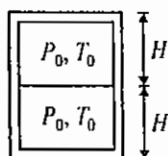
$\Rightarrow T_2 = \sqrt{2} T_1.$

Correct option is (b)

- Q. A frictionless, heat conducting piston of negligible mass and the heat capacity divides a vertical, insulated cylinder of height $2H$ and cross-sectional area A into two halves. Each half contains one mole of an ideal gas at temperature T_0 and pressure P_0 corresponding to STP. The heat capacity ratio $\gamma = C_p / C_v$ is given. A load of weight W is tied to the piston and suddenly released. After the system comes to equilibrium, the piston is at rest and the temperature of the gases in the two compartments are equal. What is the final displacement y of the piston from its initial, assuming $\gamma W \gg T_0 C_v$? [JEST 2018]

- (a) $\frac{2H}{\sqrt{\gamma}}$ (b) $H\gamma$ (c) $\frac{H}{\sqrt{\gamma}}$ (d) $\frac{2H}{\gamma}$

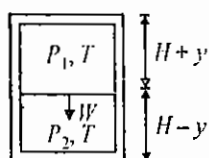
Soln. Initial condition:



The ideal gas equation gives

$$P_0 A H = R T_0$$

Final condition:



The ideal gas equation gives

$$P_1 A (H+y) = R T \quad \text{and} \quad P_2 A (H-y) = R T$$

The condition for equilibrium of piston gives

$$P_1 + \frac{W}{A} = P_2$$

$$\Rightarrow \frac{RT}{A(H+y)} + \frac{W}{A} = \frac{RT}{A(H-y)}$$

$$\Rightarrow \frac{2RTy}{H^2 - y^2} = W$$

Moreover, the first law of thermodynamics gives

$$dU_1 + dU_2 - W y = 0$$



$$\Rightarrow nC_V(T - T_0) + nC_V(T - T_0) = Wy$$

$$\Rightarrow 2nC_V T = Wy, \text{ where } Wy \gg T_0 C_V$$

$$\Rightarrow W = \frac{2nC_V T}{y}$$

$$\Rightarrow \frac{2RTy}{H^2 - y^2} = \frac{2RT}{(\gamma - 1)y} \Rightarrow y = \frac{H}{\sqrt{\gamma}}$$

Correct option is (c)

- Q. In an experiment, certain quantity of an ideal gas at temperature T_0 , pressure P_0 and volume V_0 is heated by a current flowing through a wire for a duration of t seconds. The volume is kept constant and the pressure changes to P_1 . If the experiment is performed at constant pressure starting with the same initial conditions, the volume changes from V_0 to V_1 . The ratio of the specific heats at constant pressure and constant volume is

- (a) $\frac{P_1 - P_0}{V_1 - V_0} \frac{V_0}{P_0}$ (b) $\frac{P_1 - P_0}{V_1 - V_0} \frac{V_1}{P_1}$ (c) $\frac{P_1 V_1}{P_0 V_0}$ (d) $\frac{P_0 V_0}{P_1 V_1}$ [JEST 2018]

Soln. If the volume is kept constant

$$dQ_V = dU = \frac{f}{2} nRdT = \frac{f}{2} (VdP)$$

$$\therefore \Delta Q_V = \frac{f}{2} V_0 (P_1 - P_0)$$

If the pressure is constant,

$$dQ_P = nC_P dT = \left(\frac{f}{2} + 1 \right) nRdT = \left(\frac{f}{2} + 1 \right) (PdV)$$

$$\therefore \Delta Q_P = \left(\frac{f}{2} + 1 \right) P_0 (V_1 - V_0)$$

If both the processes are same, the same amount of heat flows. So,

$$\Delta Q_V = \Delta Q_P$$

$$\Rightarrow \frac{f}{2} V_0 (P_1 - P_0) = \left(\frac{f}{2} + 1 \right) P_0 (V_1 - V_0)$$

$$\Rightarrow 1 + \frac{2}{f} = \frac{V_0 (P_1 - P_0)}{P_0 (V_1 - V_0)} \quad \text{where, } 1 + \frac{2}{f} = \gamma$$

$$\therefore \gamma = \frac{P_1 - P_0}{V_1 - V_0} \frac{V_0}{P_0}$$

Correct option is (a)

- Q. An ideal fluid is subjected to a thermodynamic process described by $\rho = CV^{-\alpha}$ and $P = n\rho^\Gamma$, where ρ is energy density and P is pressure. For what values of n and Γ , the process is adiabatic if the volume is changed slowly? [JEST 2018]

- (a) $\Gamma = \alpha - 1, n = 1$ (b) $\Gamma = 1 - \alpha, n = \alpha$ (c) $\Gamma = 1, n = \alpha - 1$ (d) $\Gamma = \alpha, n = 1 - \alpha$

Soln. Given: $\rho = \frac{U}{V} = CV^{-\alpha}$ or $U = CV^{-\alpha+1}$



And $P = n\gamma^{\Gamma} = n\left(\frac{U}{V}\right)^{\Gamma} = n(CV^{-\alpha})^{\Gamma}$

From first law of thermodynamics, we have

$$dQ = dU + PdV$$

For adiabatic process, we have

$$dQ = 0$$

$$\Rightarrow dU + PdV = 0$$

$$\Rightarrow d(CV^{-\alpha+1}) + nC^{\Gamma}V^{-\alpha\Gamma}dV = 0$$

$$\Rightarrow C(-\alpha+1)V^{-\alpha}dV + nC^{\Gamma}V^{-\alpha\Gamma}dV = 0$$

$$\Rightarrow C(1-\alpha)V^{-\alpha} = -nC^{\Gamma}V^{-\alpha\Gamma}$$

$$\Rightarrow (\alpha-1) = nC^{\Gamma-1}V^{-\alpha(\Gamma-1)}$$

On comparing, we have

$$n = \alpha - 1 \text{ and } \Gamma - 1 = 0$$

Or, $n = \alpha - 1 \text{ and } \Gamma = 1$

Correct option is (c)



Chapter 3

Laws of thermodynamics & their Consequences-2

Second law of Thermodynamics

The 1st law of thermodynamics tells that energy of the universe remain constant. This law tell us that heat and mechanical work both are interconvertible. It doesn't tell us the limitation and condition for this conversion i.e how much heat is converted into work and whether the transformation itself can take place or not (The direction of transformation). Thus 1st law simply tells that if a process take place, energy will remain conserve. It doesn't tell us whether, the process is possible or not. The condition of transformation of heat into work (whether the process is possible or not) is specified by the 2nd law of thermodynamics. There are two equivalent statements of 2nd law of thermodynamics.

Kelvin – Plank Statement: It is impossible for a self acting device or machine unadded by any external agency to convert heat from a cold body to a hot body or heat can't flow spontaneously from a cold body to a hot body. Kelvin Plank and Clausius statement are equivalent. Any process which violates Kelvin Plank statement also violate Clausius statement. Any process which violate Kelvin-Plank and Clausius statement would also violate the principle of increase in entropy

$$(\Delta S)_{\text{universe}} \geq 0$$

$$\rightarrow \Delta S = 0 \quad \text{for Reversible process}$$

$$\Delta S > 0 \quad \text{for irreversible or natural process.}$$

$$dS = \frac{dQ}{T} \quad \text{Mathematical form of 2nd law of thermodynamics}$$

$$\text{For reversible process } \Delta S = \oint \frac{dQ}{T} = 0$$

The entropy of an isolated system can never decrease - entropy of a system measures the disorder of the system

Carnot Theorem

1st Statement : All the reversible engine working between source and sink have the same efficiency whatever the working substance

$$e_{R1} = e_{R2}$$

2nd statement : irreversible engine working between source and sink can never be more efficient then a reversible engine working between same source and sink

$$e_{R1} = e_{R2} > e_1$$

entropy of an isolated system can never decrease.

Complete conversion of work into heat is possible but the reverse is not possible.

Heat engine:

A cyclic device that converts heat taken from the source into mechanical work is called a heat engine.



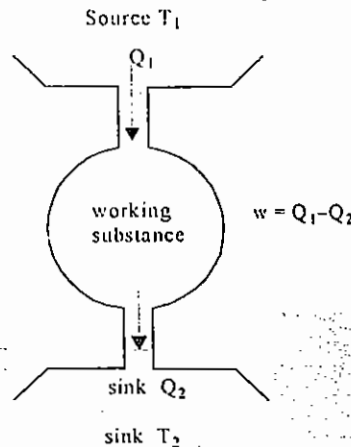
Parts of the engine : (i) Source (ii) Sink (iii) working substance.

The net amount of work done by the substance $W = Q_1 - Q_2$

Efficiency : Efficiency of a heat engine is defined as the ratio of the work obtained to heat taken in from the source in one cycle.

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$\eta = 1$ when $Q_2 = 0$ i.e. the sink is at absolute Zero which is impossible.



Indicator diagram :

The resultant PV diagram of a system undergoing a process is called indicator diagram. This diagram enables us to represent the working of an engine and to calculate useful work from the system (engine)

Reversible engine :

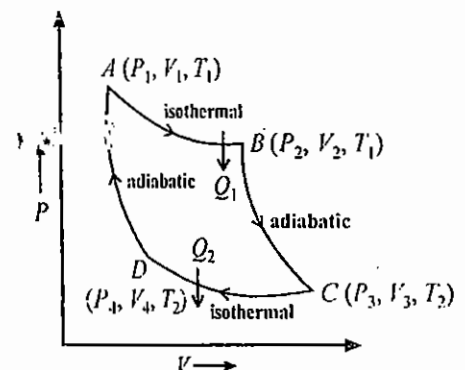
The engine based on reversible cycle is called reversible engine (Carnot reversible engine).

- (i) A cylinder with perfectly heat insulating walls but perfectly conducting base and closed with a tight fitting perfectly insulating and frictionless piston, filled with fixed mass of perfect gas as a working substance.
- (ii) A hot body of infinitely large heat capacity at constant temperature T_1 (source)
- (iii) A cold body of infinitely large heat capacity at constant temperature T_2 (sink)
- (iv) A perfectly heat insulating stand.

Q_1 = heat taken from the source during Process AB

Q_2 = heat given to the sink from the system during process CD

$$\text{Carnot's Cycle} \left\{ \begin{array}{l} W_{AB} = Q_1 = \mu R T_1 \log \frac{V_2}{V_1} \\ W_{CD} = Q_2 = \mu R T_2 \log \frac{V_3}{V_4} \\ W_{BC} = \frac{\mu R}{\gamma - 1} (T_2 - T_1) \\ W_{DA} = \frac{\mu R}{\gamma - 1} (T_2 - T_1) \end{array} \right.$$



$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = \mu R T_1 \log \frac{V_2}{V_1} + \mu R T_2 \log \frac{V_3}{V_4}$$



Efficiency

$$\eta = \frac{W}{Q} = 1 - \frac{Q_2}{Q_1} \quad \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \log \frac{\frac{V_3}{V_4}}{\frac{V_2}{V_1}}$$

Since the curve BC and DA represents adiabatic expansion and compression respectively.

$$TV^{\gamma-1} = \text{Const}$$

$$\text{So} \quad T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad \dots (i)$$

$$\text{and} \quad T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1} \quad \dots (ii)$$

$$\text{Dividing (i)/(ii), } \frac{V_2}{V_1} = \frac{V_3}{V_4} \Rightarrow \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\text{So} \quad \eta = 1 - \frac{Q_2}{Q_1} \quad \text{or} \quad \eta = 1 - \frac{T_2}{T_1}$$

Refrigerator

A device that remove heat from a cold body and adding it to a hot body with the help of external agency. It is the reverse of heat engine.

Co-efficient of performance of a refrigerator :

It is the ratio heat taken in from the cold body to work done by external device need to run the refrigerator

$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

$$\text{But we know} \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

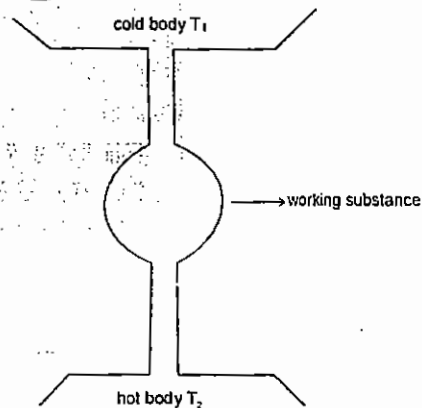
$$\text{So} \quad K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

Relation between efficiency of a carnot engine (η) and co-efficient of performance (K) :

$$\eta = \frac{T_1 - T_2}{T_1} \quad \text{and} \quad K = \frac{T_2}{T_1 - T_2}$$

$$\text{Now} \quad K + 1 = \frac{T_1}{T_1 - T_2} \Rightarrow \frac{1}{K + 1} = \frac{T_1 - T_2}{T_1} = \eta$$

$$\boxed{\eta = \frac{1}{K + 1}}$$



A good refrigerator should have a high co-efficient of performance.



Entropy

One of the most common interpretation of entropy is done by saying that the entropy is the measure of disorderness of the system. It means more the orderness is present in the system less will be its entropy. Similarly, more the disorderness present in the system more will be its entropy. For example : The entropy of boiling water is more than the entropy of ice. Also, one of the common means for knowing the change in entropy of the system (for spontaneous-irreversible processes), is that the change in entropy will always be positive i.e., for irreversible spontaneous process the *entropy of the universe* always increases.

Mathematically the change in entropy for a reversible process is defined as

$$dS = \frac{dQ_R}{T}$$

$$\Rightarrow \int_{S_i}^{S_f} dS = \int_i^f \frac{dQ}{T} \quad \Rightarrow \quad \Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

In the above definition S is an exact differential. It means that just like internal energy the entropy is also state function. For the case of irreversible process, the change in entropy is calculated by replacing the irreversible process with a reversible process between the same initial and final states.

In order to understand the physical meaning of entropy and its significance, it is necessary to study *all* the entropy changes that take place when a system undergoes a reversible process. If we calculate the entropy change of the system and add the calculated entropy change of the surroundings, then we obtain the sum of the entropy changes brought about by this particular process. We may call this sum the *entropy change of the universe* due to the process in question.

The following table shows the calculation of change in entropy for various irreversible processes.

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal energy of a reservoir	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system	$C_p \ln \frac{T_f}{T_i}$	0	$C_p \ln \frac{T_f}{T_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas	$nR \ln \frac{V_f}{V_i}$	0	$nR \ln \frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hotter to a cooler reservoir	0	$\frac{Q}{T_2} - \frac{Q}{T_1}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases	$2nR \ln \frac{V_f}{V_i}$	0	$2nR \ln \frac{V_f}{V_i}$



Isoentropic process : A reversible process during which the entropy of a system remains constant is called isoentropic process.

According to 2nd law of thermodynamics $dQ = TdS$

For adiabatic process $dQ = 0 \Rightarrow dS = 0 \Rightarrow S = \text{constant}$

A reversible adiabatic process is an isoentropic process for irreversible process $dS > 0$.

Q. From the law of thermodynamics prove the following relation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ and hence show

that the

internal energy of an ideal gas is independent of its volume but not so for an actual gas.

Soln. 1st law of thermodynamics $dQ = dU + PdV$
 2nd law of thermodynamics $dQ = TdS$
 Combining these two laws $TdS = dU + PdV$

$$\Rightarrow dS = \frac{1}{T} dU + \frac{P}{T} dV$$

Hence we can write at constant temperature

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \Rightarrow T \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P$$

Using Maxwell's thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ the above equation become

$$T \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P \quad \text{so} \quad \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \dots (i)$$

Now, from equation (i), we have

$$PV = RT \Rightarrow P = \frac{RT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

Put this value in eqn (i)

$$\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{R}{V} - P \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \quad \left(\because \frac{RT}{V} = P\right)$$

Hence internal energy of an ideal gas is independent of volume

$$(ii) \quad \left(P + \frac{a}{V^2}\right)(V - b) = RT \quad P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \frac{\partial P}{\partial T} = \frac{R}{V - b}$$

Put this value in eqn (i)

$$\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{R}{V - b} - P = \frac{a}{V^2}$$

Hence internal energy of an real gas depends on volume. (All the above treatment is done for 1 mole of gas).

Q. The mass M of a liquid at temperature T_1 is mixed with an equal mass of same liquid at temperature T_2 . The system is thermally insulated. Show that the entropy change of the universe is

$$2MC_p \log_e \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$$

Soln. When M gm of the liquid at temperature T_1 is mixed with an equal mass of same liquid at temp T_2 the tempera-

ture of the mixture will be $\frac{T_1 + T_2}{2}$



Now change in entropy when the temp of one gm of liquid changes from T_1 to $\frac{T_1+T_2}{2}$

$$\Delta S_1 = \int_{T_1}^{\frac{T_1+T_2}{2}} \frac{dQ}{T} = \int_{T_1}^{\frac{T_1+T_2}{2}} MC_P \frac{dT}{T} = MC_P \log_e \frac{T_1+T_2}{2T_1}$$

Also the change in entropy when the temp of M gm of liquid changes from T_2 to $\frac{T_1+T_2}{2}$

$$\Delta S_2 = \int_{T_2}^{\frac{T_1+T_2}{2}} MC_P \frac{dT}{T} = MC_P \log_e \frac{T_1+T_2}{2T_2}$$

Hence the entropy change of the universe

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 \\ &= MC_P \log_e \frac{T_1+T_2}{2T_1} + MC_P \log_e \frac{T_1+T_2}{2T_2} \\ &= MC_P \log_e \left[\frac{T_1+T_2}{2T_1} \times \frac{T_1+T_2}{2T_2} \right] \\ &= MC_P \log_e \left(\frac{T_1+T_2}{2\sqrt{T_1T_2}} \right)^2 \end{aligned}$$

$$\Delta S = 2MC_P \log_e \frac{T_1+T_2}{2\sqrt{T_1T_2}}$$

which is necessarily +ve.

Q. For an isobaric process prove the relation

$$(i) \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial S}{\partial T} \right)_P = - \left(\frac{\partial P}{\partial T} \right)_S \quad (ii) \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial P}{\partial T} \right)_V$$

Soln. In the set of four thermodynamic variable (P, V, T, S) only two are independent variables while other two may be expressed as their functions.

We can represent pressure P as the function of two independent variables S and T i.e.

$$P = P(S, T) \Rightarrow dP = \left(\frac{\partial P}{\partial S} \right)_T dS + \left(\frac{\partial P}{\partial T} \right)_S dT$$

For an isobaric process $dP = 0$

Hence

$$\left(\frac{\partial P}{\partial S} \right)_T dS + \left(\frac{\partial P}{\partial T} \right)_S dT = 0$$

$$\left(\frac{\partial P}{\partial S} \right)_T dS = - \left(\frac{\partial P}{\partial T} \right)_S dT$$

$$\left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial S}{\partial T} \right)_P = - \left(\frac{\partial P}{\partial T} \right)_S$$

(ii) Again we represent the pressure as the function of T and V

$$P = P(T, V)$$

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV$$

For an isobaric process $dP = 0$



$$\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T dV = -\left(\frac{\partial P}{\partial T}\right)_V dT$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

Q. Prove the thermodynamic relation

(i) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

(ii) $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

Soln. (i) Let the entropy S of a thermodynamic system be a function of temperature T and volume V i.e.

$$S \equiv S(T, V)$$

Since dS is a perfect differential, we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying by T , we have

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \dots (i)$$

Since $TdS = dQ$

For any substance the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

From Maxwell's first relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Making these substitution in eqn (i)

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \rightarrow \text{Required relation}$$

(ii) Let the entropy S of a thermodynamic system be function of temperature T and pressure P i.e.

$$S = S(T, P)$$

Since dS is a perfect differential, we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying by T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad \dots (ii)$$

For any substance the specific heat at constant pressure is

$$\text{given by } C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$



From Maxwell's IInd relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

making these substitution in equation (ii)

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

Q. Find the efficiency of the Carnot engine working between the steam point and the ice point.

Soln. Given $T_1 = 100^\circ\text{C} = 100 + 273 = 373 \text{ K}$ $T_2 = 0^\circ\text{C} = 0 + 273 = 273 \text{ K}$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{373 - 273}{373} = \frac{100}{373}$$

$$\% \text{ of efficiency} = \frac{100}{373} \times 100 = 26.81\%$$

Q. A carnot engine whose temperature of the source is 400 K takes 300 calories of heat at this temperature and reject 150 calories of heat to the sink. What is temperature of the sink. Also calculate the efficiency of the engine?

Soln. $H_1 = 200 \text{ Cal}$, $H_2 = 150 \text{ Cal}$, $T_1 = 400 \text{ K}$, $T_2 = ?$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2} \Rightarrow T_2 = \frac{H_2}{H_1} \times T_1 = \frac{150}{200} \times 400 = 300 \text{ K}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$$

$$\% \text{ of efficiency} = 0.25 \times 100 = 25\%$$

Q. A carnot engine is operated between two reservoirs at temperature of 450 K and 350 K. If the engine receives 1000 calories of heat from the source in each cycle. Calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine & the work done by the engine in each cycle (1 calorie = 4.2J)

Soln. $T_1 = 450^\circ\text{K}$, $T_2 = 350^\circ\text{K}$, $H_1 = 1000 \text{ cal}$, $H_2 = ?$

$$\frac{H_2}{T_2} = \frac{H_1}{T_1} \Rightarrow H_2 = \frac{T_2}{T_1} \times H_1 = \frac{350}{450} \times 1000 = 777.77 \text{ cal}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{350}{450} = \frac{100}{450} = 0.2222$$

$$\% \text{ of efficiency} = 22.22\%$$

$$\text{work done in each cycle} = H_1 - H_2$$

$$= 1000 - 777.77 \text{ Cal} = 222.23 = 222.23 \times 4.2 = 933.335 \text{ joule.}$$

Q. A carnot engine working as a refrigerator between 260 K and 300 K receives 500 calories of heat from the reservoir at the lower temperature calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of workdone in each cycle to operate the refrigerator.

Soln. $Q_1 = ?$ $Q_2 = 500 \text{ cal}$ $T_1 = 260 \text{ K}$ $T_2 = 300 \text{ K}$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \Rightarrow Q_1 = \frac{Q_2}{T_2} \times T_1 = \frac{500 \times 260}{300} = 576.92 \text{ cal}$$

$$W = Q_1 - Q_2 = 76.92 \text{ cal} = 76.92 \times 4.2 = 323.08 \text{ joule.}$$



- Q.** A carnot's refrigerator takes heat from water at 0°C and discard it to a room at 27°C . 1 kg of water at 0°C is to be changed into ice at 0°C . How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the co-efficient of performance of the machine?

Soln. $Q_1 = ?$ $Q_2 = 1000 \times 80 = 80,000 \text{ cal.}$ $L = 80 \text{ Cal/g (Latent heat of ice)}$

$$T_1 = 300\text{K} \quad T_2 = 273^\circ\text{K}$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_1 = \frac{T_1}{T_2} \times Q_2 = \frac{300}{273} \times 80,000 = 87,900 \text{ cal.}$$

Work done by the refrigerator

$$W = J(Q_1 - Q_2) = 4.2(87900 - 80000) \\ = 4.2 \times 7900 = 3.183 \times 10^4 \text{ J}$$

$$\text{Co-efficient of performance} = \frac{Q_2}{Q_1 - Q_2} = \frac{80,000}{87900 - 80,000} = \frac{80,000}{7900} = 10.13$$

- Q.** A carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased.

Soln. $\eta = 50\% = 0.5$, $T_2 = 273 + 7 = 280 \text{ K}$, $T_1 = ?$

$$\eta = 1 - \frac{T_2}{T_1} = 0.5 = 1 - \frac{280}{T_1}$$

$$\frac{280}{T_1} = 0.5 \Rightarrow T_1 = \frac{280}{0.5} = \frac{2800}{5} = 560 \text{ K}$$

In the 2nd case

$$\eta' = 70\% = 0.7$$

$$T_2 = 280\text{K}, \quad T_1 = ?$$

$$\eta' = 1 - \frac{T_2}{T_1}$$

$$0.7 = 1 - \frac{280}{T_1} \Rightarrow \frac{280}{T_1} = 0.3 \Rightarrow T_1 = \frac{280}{0.3} = 933.33 \text{ K}$$

So increase in temperature = $933.33 - 560 = 372.33 \text{ K}$.

- Q.** In a Carnot cycle, isothermal expansion of an ideal gas take place at 400 K and the isothermal compression at 300 K . During the expansion 500 cal of heat energy are transfered to the gas. Determine

- (1) The work performed by the gas during isothermal expansion.
- (2) The heat rejected from the gas during an isothermal compression
- (3) The work done in isothermal compression of gas

Soln. (1) The work performed by the gas during the isothermal expansion is equivalent to heat Q_1 absorbed by the gas

$$\text{Here, } Q_1 = W = 500 \text{ cal}$$

(2) Let Q_2 be the amount of heat rejected. Then,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = 500 \times \frac{300}{400} = 375 \text{ cal}$$

(3) The work done on the gas during isothermal compression is equivalent to the heat rejected

$$W = Q_2 = 375 \text{ cal}$$



- Q.** Two identical bodies of constant heat capacities at temperature T_1 and T_2 ($T_1 > T_2$) are used as reservoirs for a heat engine. Assuming that the bodies don't undergo any phase change and remain at constant pressure P . Show that the amount of work obtained is given by

$$W = C_p (T_1 + T_2 - 2T_f)$$

where T_f is the final temperature of the bodies. Also show that W is maximum when $T_f = \sqrt{T_1 T_2}$

- Soln.** The working substance takes heat from the body at temperature T_1 and after doing work gives the balance heat to the body at temperature T_2 . This process continues until T_1 drops to T_f and T_2 rises to T_f . The total heat taken from the hot body

$$Q_1 = C_p (T_1 - T_f) \quad \dots (i)$$

heat given to the cold body

$$Q_2 = C_p (T_f - T_2) \quad \dots (ii)$$

The balance $(Q_1 - Q_2)$ converts into work

$$W = Q_1 - Q_2 = C_p (T_1 - T_f) - C_p (T_f - T_2) \Rightarrow W = C_p (T_1 - T_f - T_f + T_2) = C_p (T_1 + T_2 - 2T_f)$$

The heat Q_1 is taken in at a mean temperature $= \frac{T_1 + T_f}{2}$

heat Q_2 is given out at a mean temperature $= \frac{T_2 + T_f}{2}$

Carnot engine have max efficiency so the work done must be maximum

$$\frac{Q_1}{Q_2} = \frac{\frac{T_1 + T_f}{2}}{\frac{T_2 + T_f}{2}} = \frac{T_1 + T_f}{T_2 + T_f}$$

From equation (i) and (ii)

$$\frac{Q_1}{Q_2} = \frac{T_1 - T_f}{T_f - T_2}$$

$$\text{So } \frac{T_1 + T_f}{T_2 + T_f} = \frac{T_1 - T_f}{T_f - T_2} \Rightarrow T_f = \sqrt{T_1 T_2}$$

- Q.** In a Carnot cycle, isothermal expansion of an ideal gas take place at 400 K and the isothermal compression at 300 K. During the expansion 500 cal of heat energy are transferred to the gas. Determine

- (1) The work performed by the gas during isothermal expansion.
- (2) The heat rejected from the gas during an isothermal compression
- (3) The work done in isothermal compression of gas

- Soln.** (1) The work performed by the gas during the isothermal expansion is equivalent to heat Q_1 absorbed by the gas

$$\text{Here } Q_1 = 500 \text{ cal} = W \\ W = 500 \times 4.18 = 2090 \text{ Joule.}$$

- (2) Let Q_2 be the amount of heat rejected

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = 500 \times \frac{300}{400} = 375 \text{ K}$$

- (3) The work done on the gas during isothermal compression is equivalent to the heat rejected

$$W = Q_2 = 375 \text{ cal} = 375 \times 4.18 = 1567.5 \text{ joule}$$

- Q.** A reversible engine workes between two temperature whose difference is 100°C . If 746 J of heat from the source is taken and 546 J heat is given to the sink by working substance. Calculate the temperature of the source and sink?

- Soln.** Given $T_1 - T_2 = 100$ $Q_1 = 746$, $Q_2 = 546$



use $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{Q_1}{Q_2} = \frac{746}{546} = \frac{373}{273}$

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \Rightarrow \frac{200}{546} = \frac{100}{T_2} \Rightarrow T_2 = \frac{546 \times 100}{200} = 273$$

Now $T_1 - T_2 = 100 \Rightarrow T_1 = T_2 + 100 = 273 + 100 = 373.$

- Q.** An ideal carnot heat engine takes 100 cal of heat at 627°C from a source and rejects a part at 27°C to the sink. Find the work done by the engine per cycle, the heat rejected to the sink per cycle & the efficiency of the engine.

Soln. $Q_1 = 100 \text{ cal}$ $T_1 = 627^\circ\text{C}$
 $Q_2 = ?$ $T_2 = 27^\circ\text{C}$

Let the temperature of the sink = x

Now $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{100}{x} = \frac{627}{27} \Rightarrow x = \frac{1000 \times 27}{627} = 333.3 \text{ cal}$

So the heat reject per cycle to the sink = 333.3 cal

Now $W = Q_1 - Q_2 = 1000 - 333.3 = 666.7 \text{ cal}$

Now, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{27}{627} = \frac{600}{627} = \frac{200}{209}$

- Q.** The efficiency of a carnot cycle is $\frac{1}{6}$, on reducing the temperature of the sink by 65°C the efficiency increases to $\frac{1}{3}$. Find the initial and final temperature between which the cycle it is working

Soln. $1 - \frac{T_2}{T_1} = \frac{1}{6} \Rightarrow \frac{T_1 - T_2}{T_1} = \frac{1}{6} \Rightarrow 6T_1 - 6T_2 = T_1 \text{ or } 5T_1 - 6T_2 = 0 \quad \dots (i)$

Now, $1 - \frac{(T_2 - 65)}{T_1} = \frac{1}{3} \Rightarrow \frac{T_1 - T_2 + 65}{T_1} = \frac{1}{3} \Rightarrow 3T_1 - 3T_2 + 195 = T_1$

$\Rightarrow 2T_1 - 3T_2 = -195 \quad \dots (ii)$

Solving eqn (i) and (ii)

$5T_1 - 6T_2 = 0$

$2T_1 - 3T_2 = -195$

Solving, we have

$T_1 = 390 \text{ K and } T_2 = 325 \text{ K}$

- Q.** On a winter day, when the temperature outside is 17°C the temperature inside a room is maintained at 27°C by using a heat pump. The heat pump compensates for the loss of heat due to the difference of temperature. If, for the temperatures given, the rate of heat loss is 6000 cal/s, what is the minimum rate of consumption of energy by the pump?

(a) 840 watt (b) 9300 watt (c) 15000 watt (d) 200 watt (e) 430 watt

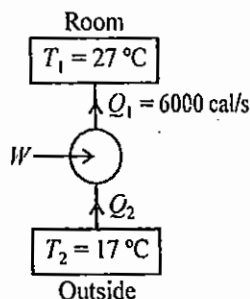
Soln. For minimum rate of consumption, the engine must be based on Carnot cycle and hence

$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$

$\therefore Q_2 = \frac{290}{300} \times 6000 = 5800 \text{ cal/s}$

$\therefore W_{\min} = Q_1 - Q_2 = 200 \text{ cal/s} = 840 \text{ W}.$

Correct option is (a)





Q. Two carnot engines are operating in series. The 1st engine absorbs a quantity of heat Q_1 at a temperature T_1 and after doing work W_1 rejects the remaining heat Q_2 at lower temperature T_2 . The second engine absorbs the heat Q_2 at temperature T_2 (rejected by 1st) and after doing work W_2 rejects the remaining heat Q_3 at a still lower temperature T_3 . Compute the efficiency of the combination.

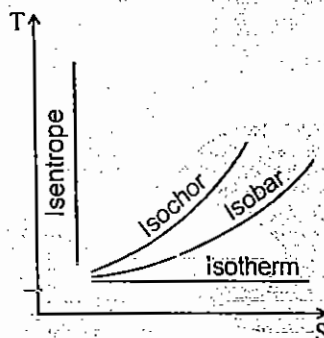
Soln. $W = (Q_1 - Q_2) + (Q_2 - Q_3) = Q_1 - Q_3$

$$\eta \text{ (efficiency)} = \frac{W}{Q_1} = \frac{Q_1 - Q_3}{Q_1} = 1 - \frac{Q_3}{Q_1}$$

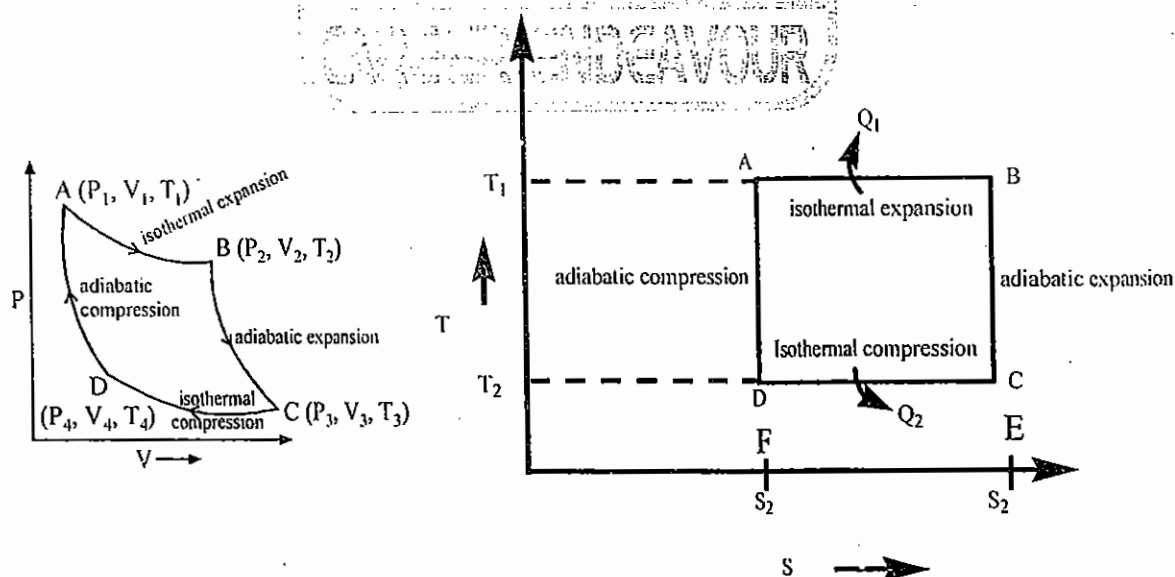
But, $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ and $\frac{Q_2}{Q_3} = \frac{T_2}{T_3}$. So, $\eta = 1 - \frac{T_3}{T_1}$.

T-S Diagram

Just like the PV-diagram is important for studying thermodynamics of an ideal gas, TS-diagram is important for studying the entropy changes taking place in various processes. The following figures schematically show the entropy changes taking place in various processes with the help of TS-curves.

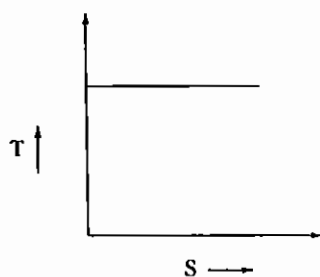


T-S Curve for Carnot Engine :

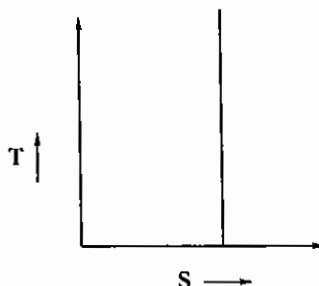


Area under PV curve represents amount of work done. Area of the cycle on T - S curve represent heat transfer.

$$\eta = \frac{W}{Q} = \frac{\text{Area of ABCD}}{\text{Area of ABEF}}$$

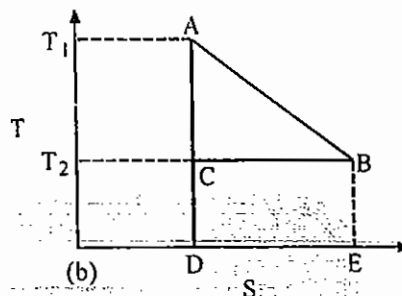
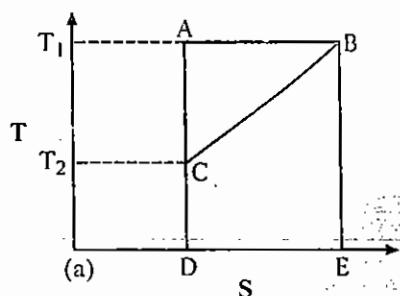


(Isothermal)



(Isentropic)

Q. Compare the efficiency of the following cycles : →



Soln. If Q_1 be the amount of heat absorbed during the process in which entropy increases and Q_2 be the amount of heat rejected during the process in which entropy decreases

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\text{Area of } ABC}{\text{Area of } ABED}$$

Area of ABC for fig (a) = Area of ABC for fig (b)

Area of ABED for fig (a) > Area of ABED for fig (b)

$$\Rightarrow \eta_a < \eta_b$$

Slope in T-S diagram:

In a T-S diagram the slope of an isochoric process = $\frac{T}{C_V}$

In a T-S diagram the slope of an isobaric process = $\frac{T}{C_P}$

$$\frac{\text{Slope of isochoric}}{\text{Slope of isobaric}} = \frac{T/C_V}{T/C_P} = \frac{C_P}{C_V} = \gamma$$

Q. Calculate the change in entropy when an ideal gas undergoes reversible isothermal expansion from initial volume V_i to final volume V_f .

Soln. $dQ = TdS \Rightarrow dS = \frac{dQ}{T}$

$$\Delta S = S_f - S_i = \int_{V_i}^{V_f} \frac{dQ}{T}$$

According to first law of thermodynamics $dQ = dU + dW$

$dU = 0$ because the process is reversible-isothermal expansion

$$dQ = dW = PdV$$



$$\text{So } \Delta S = \int_{V_i}^{V_f} \frac{P dV}{T}$$

$$\text{But we know } PV = \mu RT \Rightarrow \frac{P}{T} = \frac{\mu R}{V}$$

$$\Delta S = \int_{V_i}^{V_f} \frac{\mu R}{V} dV = \mu R [\ln V]_{V_i}^{V_f} = \mu R \ln \frac{V_f}{V_i}$$

Q. Calculate the change in entropy when a liquid is heated from T_1 to T_2 ($T_2 > T_1$).

Soln. Let a liquid of mass m specific heat C is heated from T_1 to T_2 .

If dQ is the amount of heat taken by the liquid to rise its temperature by dT then

$$dQ = mCdT$$

Corresponding change in entropy

$$dS = \frac{dQ}{T} = \frac{mCdT}{T}$$

Entropy change in the entire process

$$(\Delta S)_{\text{liquid}} = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} mC \frac{dT}{T} = mC [\ln T]_{T_1}^{T_2}$$

$$(\Delta S)_{\text{liquid}} = mC \ln \frac{T_2}{T_1}$$

Which is +ve ($\because T_2 > T_1$). Thus entropy of liquid increases.

Change in entropy on cooling :

$$\Delta S = mC \ln \frac{T_2}{T_1}$$

Here $T_2 < T_1$ (cooling). So the entropy of the liquid decreases

Q. Calculate the change in entropy when ice (a) melts to water (b) changes into steam :

Soln. (a) when ice changes to water at 0°C the change in entropy

$$\Delta S = \int \frac{dQ}{T} = \frac{Q}{T} = \frac{ML}{T}$$

where, M = mass of liquid, L = latent heat.

(i) The change in entropy when ice is converted in water at 0°C

$$\Delta S_1 = \frac{ML}{T_1}, \text{ where } L = 80 \text{ kcal/gm}$$

The change in entropy when water is at 0°C and at 100°C

$$\Delta S_2 = mc \ln \frac{T_2}{T_1}$$

The change in entropy when water at 100°C converted into steam

$$\Delta S_3 = \frac{mL}{T_2}, \text{ where } L = 540 \text{ kcal/gm}$$

So total change in entropy

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = \frac{mL}{T_1} + mc \ln \frac{T_2}{T_1} + \frac{mL}{T_2}$$



Q. A body of mass m_1 , specific heat c_1 and temperature T_1 is thermally connected with another body of mass m_2 , specific heat c_2 and at temperature T_2 . Derive an expression for change in entropy.

Soln. Let $T_1 > T_2$ and T be the equilibrium temperature

According to the principle of calorimetry

$$m_1 c_1 (T_1 - T) = m_2 c_2 (T - T_2)$$

$$m_1 c_1 T_1 - m_1 c_1 T = m_2 c_2 T - m_2 c_2 T_2$$

$$m_1 c_1 T + m_2 c_2 T = m_1 c_1 T_1 + m_2 c_2 T_2$$

$$T = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2}$$

The change in entropy when the body comes from T_1 to T

$$\Delta S_1 = m_1 c_1 \int_{T_1}^T \frac{dT}{T} = m_1 c_1 \ln \frac{T}{T_1} \quad (T_1 > T)$$

The change in entropy when the body come from T_2 to T ($T_2 < T$)

$$\Delta S_2 = m_2 c_2 \int_{T_2}^T \frac{dT}{T} = m_2 c_2 \ln \frac{T}{T_2}$$

Total change in entropy $\Delta S = \Delta S_1 + \Delta S_2$

$$\Delta S = m_1 c_1 \ln \frac{T}{T_1} + m_2 c_2 \ln \frac{T}{T_2}$$

$$= \ln \left(\frac{T}{T_1} \right)^{m_1 c_1} + \ln \left(\frac{T}{T_2} \right)^{m_2 c_2}$$

$$\Delta S = \ln \left[\left(\frac{T}{T_1} \right)^{m_1 c_1} \left(\frac{T}{T_2} \right)^{m_2 c_2} \right] > 0$$

Q. Derive an expression for the change in entropy of a perfect gas in terms of its pressure volume and specific heat undergoing on one mole of change in state.

Soln. Let us consider one mole of perfect gas at pressure P , volume V and temperature T . When an infinitesimal amount of heat dQ is added to it the increase in entropy is

$$dS = \frac{dQ}{T}$$

From 1st law $dQ = dU + dW$

$$\text{But } dU = C_V dT \quad \text{and} \quad dW = PdV = RT \frac{dV}{V}$$

$$\text{so } dQ = C_V dT + RT \frac{dV}{V}$$

$$dS = \frac{dQ}{T} = C_V \frac{dT}{T} + R \frac{dV}{V}$$

The total change in entropy

$$S = \int \frac{dQ}{T} = C_V \int \frac{dT}{T} + R \int \frac{dV}{V} \quad \dots (i)$$

From ideal gas eqn. $PV = RT$

$$dT = \frac{PdV + VdP}{R}$$



$$\text{and } R = C_p - C_v$$

$$\begin{aligned} \therefore S &= C_v \int \frac{PdV + VdP}{RT} + R \int \frac{dV}{V} \\ &= C_v \int \frac{PdV + VdP}{pV} + (C_p - C_v) \int \frac{dV}{V} \\ &= C_v \int \frac{dV}{V} + C_v \int \frac{dP}{P} + C_p \int \frac{dV}{V} - C_v \int \frac{dV}{V} \\ &= C_v \int \frac{dP}{P} + C_p \int \frac{dV}{V} \end{aligned}$$

$$S = C_v \log P + C_p \log V + \text{constant}$$

If a gas passes from an initial state P_i, V_i, T_i to P_f, V_f, T_f then the change in entropy of the gas is

$$\Delta S = C_v \log \frac{P_f}{P_i} + C_p \log \frac{V_f}{V_i}$$

Q. Derive an expression for change in entropy of a perfect gas in terms of its temperature, pressure and specific heat at constant pressure.

Soln. $dQ = dU + dW = C_v dT + PdV = C_v dT + RT \frac{dV}{V} = TdS$

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V}$$

$$\Delta S = \int_i^f dS = \int_i^f \frac{C_v dT}{T} + R \int_i^f \frac{dV}{V} = C_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$$

Again $\frac{PV}{T} = \text{const} \Rightarrow \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \Rightarrow \frac{V_f}{V_i} = \frac{P_i T_f}{P_f T_i}$

$$\begin{aligned} \Delta S &= C_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i} = C_v \ln \frac{T_f}{T_i} + R \ln \frac{P_i}{P_f} + R \ln \frac{T_f}{T_i} \\ &= C_v \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i} + R \ln \frac{T_f}{T_i} \\ &= (C_p - R) \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i} + R \ln \frac{T_f}{T_i} \\ &= C_p \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i} \end{aligned}$$

Q. Calculate the change in entropy of a vander Waals' gas as its state changes from (V_i, T_i) to (V_f, T_f) where equation of state for one mole of vander Waals' gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ where } a, b \text{ are vander Waals' constants}$$

Soln. $dS = \frac{dQ}{T}$: (2nd law of thermodynamics)

$dQ = dU + dW$: (1st law of thermodynamics)

$$dU = C_v dT + \frac{a}{V^2} dV \text{ and } dW = PdV = \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) dV$$



$$\text{So, } dS = \frac{dU + dW}{T} = \frac{C_V dT + \frac{RT}{(V-b)} dV}{T} = C_V \frac{dT}{T} + R \frac{dV}{V-b}$$

The change in entropy when the gas passes from the state (V_i, T_i) to (V_f, T_f) is:

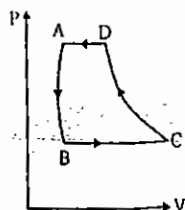
$$\begin{aligned} \Delta S = S_f - S_i &= \int_i^f dS = C_V \int_i^f \frac{dT}{T} + R \int_i^f \frac{dV}{V-b} \\ &= C_V \ln \frac{T_f}{T_i} + R \ln \frac{V_f - b}{V_i - b} \end{aligned}$$

$$\Delta S = C_V \ln \frac{T_f}{T_i} + R \ln \frac{V_f - b}{V_i - b}$$

PREVIOUS YEARS SOLUTIONS OF TIFR

Q. The pV diagram given below represents a

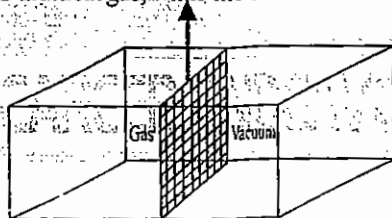
[TIFR 2010]



- (a) Carnot refrigerator
(b) Carnot engine
(c) gas turbine refrigerator
(d) gas turbine engine

Soln. The gas turbine refrigerator and the gas turbine engine is governed by two isobaric and two adiabatic process. Now since the cycle is anti-clockwise, the pV-diagram in the question represents the gas turbine refrigerator. Correct option is (c)

Q. Consider a sealed but thermally conducting container of total volume V , which is in equilibrium with a thermal bath at temperature T . The container is divided into two equal chambers by a thin but impermeable partition. One of these chambers contains an ideal gas, while the other half is a vacuum (see figure).



If the partition is removed and the ideal gas is allowed to expand and fill entire container, then the entropy per molecule of the system will increase by an amount

[TIFR 2012]

- (a) $2k_B$ (b) $k_B \ln(1/2)$ (c) $k_B \ln 2$ (d) $(k_B \ln 2)/2$

Soln. The first law of thermodynamic gives $dQ = dU + PdV$.

Since the container is in thermal equilibrium, $dU = 0$.

Therefore, $dQ = PdV$

$$\text{Therefore, } \Delta S = \int \frac{dQ}{T} = \int \frac{PdV}{T} = \int_{V/2}^V N k_B \frac{N}{V} = N k_B \ln 2.$$

So entropy change per molecule is $\Delta S = k_B \ln 2$.

Correct option is (c)



Q. A certain amount of fluid with heat capacity C_F Joules/ $^{\circ}\text{C}$ is initially at a temperature 0°C . It is then brought into contact with a heat bath at a temperature of 100°C , and the system is allowed to come into equilibrium. In this process, the entropy (in Joules/ $^{\circ}\text{C}$) of the Universe changes by [TIFR 2013]

- (a) $100C_F$ (b) 0 (c) $0.055C_F$ (d) $0.044C_F$

Soln. The heat will flow from the heat bath to the fluid which is equal to $Q = C_F(373 - 273) = 100 C_F$.

Fluid C_F	Heat bath
$T_F = 0^{\circ}\text{C}$ $= 273\text{ K}$	$T_B = 100^{\circ}\text{C}$ $= 373\text{ K}$

$$\text{Therefore, } (\Delta S)_{\text{fluid}} = \int \frac{dQ}{T} = C_F \int_{T_F}^{T_B} \frac{dT}{T} = C_F \ln \left(\frac{T_B}{T_F} \right) = C_F \ln \left(\frac{373}{273} \right)$$

$$\text{and } (\Delta S)_{\text{bath}} = \int \frac{dQ}{T} = \frac{1}{T_B} \int dQ = -\frac{Q}{T_B} = -\frac{100 C_F}{373}.$$

$$\text{Therefore, } (\Delta S)_{\text{universe}} = (\Delta S)_{\text{fluid}} + (\Delta S)_{\text{bath}} = C_F \ln \left(\frac{373}{273} \right) - \frac{100}{373} C_F = 0.044 C_F.$$

Correct option is (d)

Q. The entropy S of a black hole is known to be of the form [TIFR 2013]

$$S = \alpha k_B A$$

where A is the surface area of the black hole and α is a constant, which can be written in terms of c (velocity of light in vacuum), \hbar (reduced Planck's constant) and G_N (Newton's constant of gravitation).

Taking the radius of the black hole as $R = \frac{2G_N M}{c^2}$ it follows that the entropy S is [λ is a numerical constant]

- (a) $\frac{G_N^2 M^2 k_B}{\lambda (\hbar c)^4}$ (b) $\frac{\hbar c k_B}{\lambda G_N M}$ (c) $\frac{G_N^2 M^2 k_B}{\lambda \hbar c^4}$ (d) $\frac{G_N M^2 k_B}{\lambda \hbar c}$

Soln. Given : $S = \alpha k_B A$, where S has the same dimensions as k_B . So the dimension of α is $[M^{-2}]$.

$$\text{Letting } \alpha = c^x \hbar^y G_N^z \Rightarrow [L^{-2}] = [LT^{-1}]^x [ML^2T^{-1}]^y [M^{-1}L^3T^{-2}]^z$$

Solving, we get $x = 3$, $y = 1$ and $z = -1$.

$$\text{Therefore, } \alpha = c^3 \hbar^{-1} G_N^{-1}$$

Therefore, $S = \alpha k_B A = c^3 \hbar^{-1} G_N^{-1} k_B A$, where A is the surface area of the blackhole.

$$\text{So, } A = \beta R^2, \text{ where } \beta \text{ is some numerical constant. } \Rightarrow S = \frac{c^3 k_B}{\hbar G_N} \beta \left(\frac{2G_N M}{c^2} \right)^2 = 4\beta \frac{G_N M^2 k_B}{\hbar c}$$

$$\text{Taking } 4\beta = \frac{1}{\lambda}, \text{ we have } S = \frac{G_N M^2 k_B}{\lambda \hbar c}.$$

Correct option is (d)



PREVIOUS YEARS SOLUTIONS OF JEST

- Q.** An ideal gas with adiabatic exponent γ undergoes a process in which its pressure P is related to its volume V by the relation $P = P_0 - \alpha V$, where P_0 and α are positive constants. The volume starts from being very close to zero and increases monotonically to P_0/α . At what value of the volume during the process does the gas have maximum entropy? [JEST 2016]

(a) $\frac{P_0}{\alpha(1+\gamma)}$ (b) $\frac{\gamma P_0}{\alpha(1-\gamma)}$ (c) $\frac{\gamma P_0}{\alpha(1+\gamma)}$ (d) $\frac{P_0}{\alpha(1-\gamma)}$

Soln. From first and second law of thermodynamics, we have

$$TdS = dU + PdV$$

For maximum entropy, $dS = 0$.

$$\Rightarrow dU + PdV = 0$$

$$\Rightarrow \frac{f}{2} nR dT + PdV = 0$$

$$\Rightarrow \frac{f}{2} (PdV + VdP) + PdV = 0$$

$$\Rightarrow \left(\frac{f}{2} + 1\right) PdV + \frac{f}{2} VdP = 0$$

where $P = P_0 - \alpha V$ or $dP = -\alpha dV$

$$\text{Therefore, } \left(\frac{f}{2} + 1\right) (P_0 - \alpha V) dV + \frac{f}{2} V (-\alpha dV) = 0$$

$$\Rightarrow \left(\frac{f}{2} + 1\right) (P_0 - \alpha V) = \frac{f}{2} \alpha V \quad [\because dV \neq 0]$$

$$\Rightarrow V = \frac{\left(\frac{f}{2} + 1\right) P_0}{\left(\frac{f}{2} + 1\right) \alpha + \frac{f}{2} \alpha} = \frac{\left(\frac{f}{2} + 1\right) P_0}{(f+1)\alpha}$$

$$\text{where } \gamma = 1 + \frac{2}{f} \text{ or } f = \frac{2}{\gamma - 1}$$

$$\text{Therefore, } V = \frac{\left(\frac{1}{\gamma - 1} + 1\right) P_0}{\left(\frac{2}{\gamma - 1} + 1\right) \alpha} = \frac{\gamma}{\alpha(1 + \gamma)} P_0$$

Correct option is (c)

- Q.** A 100 ohms resistor carrying current of 1 Amp is maintained at a constant temperature of 30°C by a heat bath. What is the rate of entropy increase of the resistor? [JEST 2014]

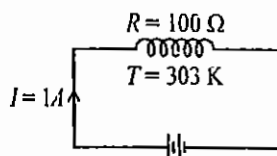
- (a) 3.3 Joules/K/sec (b) 6.6 Joules/K/sec
(c) 0.33 Joules/K/sec (d) None of the above

Soln. The change in entropy is

$$\Delta S = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{I^2 R \Delta t}{T}$$

$$\Rightarrow \frac{\Delta S}{\Delta t} = \frac{I^2 R}{T} = \frac{(1)^2 (100)}{303} = 0.33 \text{ JK}^{-1} \text{ sec}^{-1}$$

Correct option is (c)





- Q. Consider a ideal gas of mass 'm' at temperature T_1 which is mixed isobarically (i.e. at constant pressure) with an equal mass of same gas at temperature T_2 in a thermally insulated container. What is the change of entropy of the universe? [JEST 2012]

(a) $2mC_p \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right)$ (b) $2mC_p \ln \left(\frac{T_1 - T_2}{2\sqrt{T_1 T_2}} \right)$ (c) $2mC_p \ln \left(\frac{T_1 + T_2}{2T_1 T_2} \right)$ (d) $2mC_p \ln \left(\frac{T_1 - T_2}{2\sqrt{T_1 T_2}} \right)$

Soln.

$$m, T_1, C_p \quad m, T_2, C_p$$

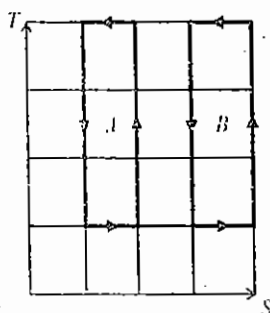
If C_p be the specific heat of the both gases and T_f be the final temperature, the principle of calorimetry gives $m_1 C_{p1} (T_f - T_1) = -m_2 C_{p2} (T_f - T_2)$, where $m_1 = m_2 = m$ and $C_{p1} = C_{p2} = C_p$.

Therefore, $T_f = \frac{T_1 + T_2}{2}$. The change in the entropy of the universe is

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_f} \frac{dQ}{T} + \int_{T_2}^{T_f} \frac{dQ}{T} = mC_p \ln \frac{T_f}{T_1} + mC_p \ln \frac{T_f}{T_2} \\ &= mC_p \ln \left(\frac{T_f^2}{T_1 T_2} \right) = mC_p \ln \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right] = 2mC_p \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right). \end{aligned}$$

Correct option is (a)

- Q. The entropy temperature diagram of two Carnot engines, A and B, are shown in the figure-5. The efficiencies of the engines are η_A and η_B , respectively. Which one of the following equalities is correct? [JEST 2015]



- (a) $\eta_A = \eta_B/2$ (b) $\eta_A = \eta_B$ (c) $\eta_A = 3\eta_B$ (d) $\eta_A = 2\eta_B$

Soln. The efficiency of a Carnot engine depends only on the temperature of the source (T_1) and of the sink (T_2) as

$$\eta = 1 - \frac{T_2}{T_1}$$

Since the values of T_1 and T_2 are same for both engines A and B, $\eta_A = \eta_B$.

Correct option is (b)

Chapter 4

Maxwell's relations & thermodynamic potentials

Maxwell's Thermodynamics Relations

From 1st law of thermodynamics

$$dQ = dU + dW \quad \dots (i)$$

where dQ is the amount of heat absorbed in reversible process

The change in entropy is given by

$$dS = \frac{dQ}{T} \quad \dots (ii)$$

From eqn (i) & (ii)

$$dU = TdS - PdV$$

So
$$\frac{\partial^2 u}{\partial y \partial x} = \frac{\partial}{\partial y} \left(T \frac{\partial S}{\partial x} - P \frac{\partial V}{\partial x} \right)$$

$$= T \frac{\partial^2 S}{\partial y \partial x} + \frac{\partial T}{\partial y} \frac{\partial S}{\partial x} - P \frac{\partial^2 V}{\partial y \partial x} - \frac{\partial P}{\partial y} \frac{\partial V}{\partial x} = T \frac{\partial^2 S}{\partial y \partial x} - P \frac{\partial^2 V}{\partial y \partial x} + \frac{\partial T}{\partial y} \frac{\partial S}{\partial x} - \frac{\partial P}{\partial y} \frac{\partial V}{\partial x}$$

Thus,
$$\frac{\partial^2 U}{\partial x \partial y} = T \frac{\partial^2 S}{\partial x \partial y} - P \frac{\partial^2 V}{\partial x \partial y} + \frac{\partial T}{\partial x} \frac{\partial S}{\partial y} - \frac{\partial P}{\partial x} \frac{\partial V}{\partial y}$$

But
$$\frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y} \quad \text{and} \quad \frac{\partial^2 S}{\partial x \partial y} = \frac{\partial^2 S}{\partial y \partial x} \quad \text{and} \quad \frac{\partial^2 V}{\partial x \partial y} = \frac{\partial^2 V}{\partial y \partial x}$$

Hence
$$\left(\frac{\partial T}{\partial y} \right)_x \left(\frac{\partial S}{\partial x} \right)_y - \left(\frac{\partial P}{\partial y} \right)_x \left(\frac{\partial V}{\partial x} \right)_y = \left(\frac{\partial T}{\partial x} \right)_y \left(\frac{\partial S}{\partial y} \right)_x - \left(\frac{\partial P}{\partial x} \right)_y \left(\frac{\partial V}{\partial y} \right)_x \quad \dots (iii)$$

1st relation : $x = T \quad y = V$

$$\frac{\partial T}{\partial x} = 1 \quad \frac{\partial V}{\partial y} = 1 \quad \frac{\partial T}{\partial y} = 0 \quad \frac{\partial V}{\partial x} = 0$$

Substituting in eqn. (iii)

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

2nd relation : $x = T \quad y = P$

$$\frac{\partial T}{\partial x} = \frac{\partial P}{\partial y} = 1 \quad \frac{\partial T}{\partial y} = \frac{\partial P}{\partial x} = 0$$

Substituting in eqn. (iii)

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

$$dS = \frac{1}{T} dQ \Rightarrow \left(\frac{\partial Q}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P$$



3rd relation : $x = S$ $y = V$

$$\frac{\partial S}{\partial x} = \frac{\partial V}{\partial y} = 1 \quad \frac{\partial S}{\partial y} = \frac{\partial V}{\partial x} = 0$$

Substituting in eqn (iii) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

or $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial Q}\right)_V}$

4th relation : $x = S$ $y = P$

$$\frac{\partial S}{\partial x} = \frac{\partial P}{\partial y} = 1 \quad \text{and} \quad \frac{\partial S}{\partial y} = \frac{\partial P}{\partial x} = 0$$

Substituting in eqn. (iii)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{or} \quad \boxed{\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial Q}\right)_P}$$

5th relation : $x = P$ $y = V$ $\frac{\partial P}{\partial x} = \frac{\partial V}{\partial S} = 1$ $\frac{\partial P}{\partial y} = \frac{\partial V}{\partial x} = 0$

Substituting in eqn (iii) $\left(\frac{\partial T}{\partial P}\right)\left(\frac{\partial S}{\partial V}\right) - \left(\frac{\partial T}{\partial V}\right)\left(\frac{\partial S}{\partial P}\right) = 1$

6th relation : $x = T$ $y = S$ $\frac{\partial T}{\partial x} = \frac{\partial S}{\partial y} = 1$ $\frac{\partial T}{\partial y} = \frac{\partial S}{\partial x} = 0$

Substituting in eqn. (iii)

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1$$

Helmholtz function or Helmholtz free energy (F)

It is also called as thermodynamical potential at constant volume. It is defined by the equation

$$F = U - TS$$

Since U , T and S are perfect differentials, F is also a perfect differential. When a system undergoes an infinitesimal reversible change from an initial equilibrium state to a final equilibrium state, the Helmholtz energy changes by an amount given by

$$\begin{aligned} dF &= dU - TdS - SdT & \text{But } dU &= TdS - PdV \\ &= TdS - PdV - TdS - SdT = -PdV - SdT \end{aligned}$$

Taking the partial differentiation of F , we have

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

Since dF is a perfect differential, we have

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \text{Maxwell's 1st relation}$$



Enthalpy or total heat function (H)

It is defined by $H = U + PV$

When a system undergoes an infinitesimal reversible change from an initial equilibrium state to a final equilibrium state, the enthalpy changes by an amount given by

$$dH = dU + PdV + VdP \quad \text{But } dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

Taking the partial differentiation of H we have

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dH is a perfect differential, we have $\left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P$

$$\text{Or} \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \rightarrow \text{Maxwell's Fourth relation}$$

Gibbs function or Gibbs free energy (G)

It is also called as thermodynamic potential at constant pressure. It is defined by

$$G = H - TS = U + PV - TS$$

For an infinitesimal reversible process, we have

$$\begin{aligned} dG &= dU + PdV + VdP - TdS - SdT \\ &= TdS - PdV + PdV + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

The partial differentiation of G gives

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Since dG is a perfect differential so we have $\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Importance :

- (1) Thermodynamic functions are of practical importance in studying the condition of equilibrium of a system e.g., the condition of equilibrium for a process in which the temperature and volume of the system remain constant (Isothermal- Isochoric) may be expressed as

$$dF = 0 \quad (\because dF = -PdV - SdT)$$

This means that out of various states which a system can assume by isothermal isochoric process, only those are stable in which the Helmholtz free energy ($F = U - TS$) is a minimum

The equation $dF = 0$ refers to a minimum value of F (and not to a maximum value). It follows from the fact that in any natural (irreversible) process the Helmholtz free energy can only fall because the entropy can only increase.

Similarly the condition of equilibrium for a process in which the temperature and pressure of the system remain constant (isothermal isobaric process) may be expressed as

$$dG = 0 \quad (\because dG = VdP - SdT)$$

This means that a system at constant temperature and pressure is in stable equilibrium when the Gibbs function G (the thermodynamic potential of constant pressure) is a minimum.



Physical significance of Helmholtz free energy : (A Helmholtz free energy)

(1) $A = U - TS \Rightarrow TS = U - A \rightarrow$ Latent energy or bound energy of the system. As it can't be used in useful form (work)

(2) For isothermal reversible process

$$-dA = PdV = dW$$

The Helmholtz free energy is the energy decrease in which $(-dA)$ gives the maximum amount of work (dW) done by the system during an isothermal change from initial state to final state. It is also called thermodynamic potential at constant volume.

$$A = U - TS \Rightarrow A = U + T \left(\frac{\partial A}{\partial T} \right)_V \rightarrow \text{Gibbs-Helmholtz relation}$$

Physical Significance of Enthalpy

(1) $dH = TdS$ (at constant P)

Enthalpy represents the quantity of heat given to the system at constant pressure. So it is called heat contained or total heat function

Physical Significance of Gibbs Function

$$dG = VdP - SdT$$

$$= -dW - SdT + PdV + VdP$$

$$-dG = dW - PdV \text{ (For isothermal isobaric process)}$$

Gibbs free energy is such that decrease in it gives the maximum non-PdV work which can be obtained from the system other than that due to change in volume for isothermal isobaric process. This is also known as thermodynamic potential at constant pressure

$$G = H - TS$$

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_P \rightarrow \text{Gibbs-Helmholtz relation.}$$

Two important derivations.

$$(i) \left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \quad (ii) \left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

(i) We know Maxwell's Relations not given in prior from Maxwell's equation.

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

Differentiating w.r.t. T at constant volume

$$\left[\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V} \right)_T \right]_V = \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

Since for a state function, second order differentials are independent of order of differentiation :

$$T \left[\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T} \right)_V \right]_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \quad (\text{multiplying with T on both sides})$$

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial Q}{\partial T} \right)_V \right]_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \quad (\because dQ = TdS)$$



$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (\text{using definition of } C_v)$$

(ii) From Maxwell's equation.

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Differentiating w.r.t. T at constant pressure

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right]_P = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Multiplying both sides by T

$$T \left[\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right]_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial Q}{\partial T}\right)_P\right]_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (\text{using definition of } C_p)$$

Q. Establish the following thermodynamic relation

$$\left(\frac{\partial Q}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$$

where α is the coefficient of volume expansion at constant pressure. Hence show that increase in pressure heats a body that expands with rise of temperature and cools that contracts on heating.

Soln. The Maxwell thermodynamic relation is:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying by T both side

$$T \left(\frac{\partial S}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P \quad (\because dQ = TdS)$$

$$\Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -TV \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha$$

where $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ is the coefficient of volume expansion

(i) If substance expands with rise in temperature then, α will be positive

$$\text{Hence } \left(\frac{\partial Q}{\partial P}\right)_T = -Ve$$

If we increase the pressure, ∂Q at constant temperature will be negative. So, to maintain temperature constant heat must be drawn from the system. It means increase in pressure will heat the system.

(ii) If substance contracts with rise in temperature then α will be negative

$$\left(\frac{\partial Q}{\partial P}\right)_T = +Ve$$

If we increase the pressure $(\partial Q)_T$ will be positive. So, to maintain temperature constant heat must be given to the system. It means increase in pressure will cool the system.



Q. Prove the Clausius-Clapeyron equation $\frac{dP}{dT} = \frac{mL}{T(V_2 - V_1)}$

Soln. The Maxwell's relation gives

$$\therefore \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

Multiplying both sides by T we get

$$T \left(\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{where } TdS = dQ$$

$$\therefore \left(\frac{\partial Q}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \dots (i)$$

Here dQ is the heat absorbed at constant temperature

$\therefore dQ$ is the latent heat

Thus if a body of mass ' m ' and latent heat ' L ' absorbs an amount of heat to change its state at constant temperature T and volumes in the 1st and the 2nd states are V_1 and V_2

Equation (i) reduces to

$$\frac{mL}{V_2 - V_1} = T \frac{dP}{dT}$$

or $\boxed{\frac{dP}{dT} = \frac{mL}{T(V_2 - V_1)}} \rightarrow \text{Clausius-Clapeyron eqn.}$

Q. The internal energy U is related to the Helmholtz free energy F by the relation:

$$(a) U = -T \left\{ \frac{\partial^2}{\partial T^2} \left(\frac{F}{T} \right) \right\}_V$$

$$(b) U = T \left\{ \frac{\partial^2}{\partial T^2} \left(\frac{F}{T} \right) \right\}_V$$

$$(c) U = -T^2 \left\{ \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right\}_V$$

$$(d) U = T^2 \left\{ \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right\}_V$$

Soln. We have

$$\begin{aligned} \left[\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_V &= \left[\frac{\partial}{\partial T} \left(\frac{U - TS}{T} \right) \right]_V \\ &= \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V - \frac{U}{T^2} - \left(\frac{\partial S}{\partial T} \right)_V \end{aligned}$$

$$\text{where } T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\text{Therefore, } U = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_V$$

Correct option is (c)



- Q. A certain system found to have a Gibbs free energy is given by $G(P, T) = RT \ln \left[\frac{aP}{(RT)^{5/2}} \right]$, where a and R are constants. Find the entropy and specific heat at constant pressure.

Soln. $G(P, T) = RT \ln \left[\frac{aP}{(RT)^{5/2}} \right]$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P = \frac{5}{2} R - R \ln \left[\frac{aP}{(RT)^{5/2}} \right]$$

$$\text{So, } C_p = \left(\frac{\partial Q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P = \frac{5R}{2}$$

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- Q. The equation of state of a gas is given by $V = \frac{RT}{P} - \frac{b}{T}$, where R is the gas constant and b is another constant parameter. The specific heat at constant pressure C_p and the specific heat at constant volume C_v for this gas is related by $C_p - C_v =$ [TIFR 2015]

- (a) R (b) $R \left(1 + \frac{RT^2}{bP} \right)^2$ (c) $R \left(1 + \frac{bP}{RT^2} \right)^2$ (d) $R \left(1 - \frac{bP}{RT^2} \right)^2$

Soln. The given equation is $V = \frac{RT}{P} - \frac{b}{T}$... (1)

Equation (1) gives,

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} + \frac{b}{T^2} = \frac{RT^2 + bP}{PT^2} \quad \dots (2)$$

Equation (1) can also be written as

$$\frac{RT}{P} = V + \frac{b}{T} = \frac{VT + b}{T} \text{ or } P = \frac{RT^2}{VT + b} \quad \dots (3)$$

$$\text{Therefore, } \left(\frac{\partial P}{\partial T} \right)_V = \frac{(VT + b)(2RT) - (RT^2)(V)}{(VT + b)^2}$$

$$= \frac{RT^2V + 2RbT}{(VT + b)^2} \quad \dots (4)$$

The general relation of $C_p - C_v$ is given by

$$C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = T \left(\frac{RT(TV + 2b)}{(TV + b)^2} \right) \left(\frac{RT + bP}{PT} \right)$$

From (3), we get

$$TV = \frac{RT^2 - Pb}{P}$$



$$\begin{aligned}\text{Therefore, } C_p - C_v &= T \left[\frac{RT \left(\frac{RT^2 - Pb}{P} + 2b \right)}{\left(\frac{RT^2 - Pb}{P} + b \right)^2} \right] \left(\frac{RT^2 + Pb}{PT^2} \right) \\ &= \left(\frac{RT + Pb}{PT} \right) \left(\frac{RT \left(\frac{RT^2 + Pb}{P} \right)}{\left(\frac{RT^2}{P} \right)^2} \right) \\ &= \left(\frac{RT^2 + Pb}{RT^4} \right) (RT^2 + Pb)^2 \\ &= \frac{1}{RT^4} (RT^2 + Pb)^2 \\ &= R \left(1 + \frac{Pb}{RT^2} \right)^2.\end{aligned}$$

Correct option is (c)

Chapter 5

Introduction to Statistical Mechanics

Thermodynamics Limit

If $N \rightarrow \infty$ $V \rightarrow \infty$

Particle density $n = \frac{N}{V}$ is fixed at a preassigned value.

Extensive property : In the thermodynamic limit the properties that become directly proportional to the size of the system (or proportional to the extensive parameters A, N, V, S, E) i.e $N \rightarrow \alpha N$, $V \rightarrow \alpha V$, $S \rightarrow \alpha S$ then such properties are called extensive properties. They have an additive nature.

Intensive property: In the thermodynamic limit the properties that become independent of the size of the system.

For example: T, P, μ (chemical potential)

Accessible microstate : The microstate which are permitted under the constraints imposed upon the system are called accessible microstate.

Thermodynamic Probability : For a given macrostate the total number of microstate is called thermodynamic Probability of that microstate.

$$S = k_B \log \omega \quad \text{or} \quad S = k_B \log \Omega$$

where ω or $\Omega \rightarrow$ Total no. of microstate for a given macrostate
(thermodynamic Probability)

Fundamental Postulate of statistical mechanics :

(equal a priori a probability) :

For a system in equilibrium, all accessible microstate corresponding to a given macrostate are equally probable i.e. probability of finding the system in all microstate for a given macrostate are equal

$$S = k_B \log \Omega \rightarrow \text{Boltzman entropy probability relation}$$

This eqn. shows the relation between macroscopic & microscopic properties or relation between thermodynamics and statistical mechanics

Random Walk: Let n_1 denote the number of steps to the right and n_2 the corresponding number of steps to the left.

Total number of steps $N = n_1 + n_2$

Net displacement $m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N$ (towards right)

If p = Probability that the step is to the right, $q = 1 - p$ = Probability that step is to the left.

Probability $W_N(n_1)$ of taking (in a total of N steps) n_1 steps to the right and n_2 steps to the left is given

$$\text{by } W_N(n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}.$$



Mean Free Path: Mean free path λ is the average distance traversed by molecule between two successive collisions. Mean free path of a molecule is related to its size. Larger its size, shorter its mean free path.

$$\lambda = \frac{1}{\sqrt{2} n \pi d^2}$$

where d = diameter of the gas molecule, n = Number of molecules per unit volume.

- Q.** A system of N particles has only two allowed state A and B. The probability for A is P and for B is $1 - P$. What is the probability for the system to be in macrostate defined by the distribution of $(r, N - r)$?

Soln. The probability of finding r particles in state A = P^r

The probability of finding $(N - r)$ particles in state B = $(1 - P)^{N-r}$

The total number of ways in which r particle can be chosen from N - particle is ${}^N C_r = \frac{N!}{r!(N-r)!}$

The probability in which r particle are in state A and $(N - r)$ particle in state

$$B = \frac{N!}{r!(N-r)!} P^r (1-P)^{N-r}$$

- Q.** A one dimensional random walker takes step to left or right with equal probability. The probability that the random walker starting from origin is back to origin after N even number of step, is

$$(i) \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^N \quad (ii) \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \quad (iii) 2N! \left(\frac{1}{2}\right)^{2N} \quad (iv) N! \left(\frac{1}{2}\right)^N$$

Soln. Probability $P = \frac{N!}{r!(N-r)!} P^r (1-P)^{N-r}$

$$= \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^{\frac{N}{2}} \left(1 - \frac{1}{2}\right)^{N - \frac{N}{2}} = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^N$$

Option (i) is correct.

- Q.** Calculate the no. of microstates for a configuration of a system of N distinguishable particles in which there are n_1 particles in state 1 & n_2 particles in state 2, n_3 particles..... n_i particle in the i th state.

Soln. Total number of particles = N

Number of microstate for state 1 = ${}^N C_{n_1}$

Number of microstate for state 2 = ${}^{N-n_1} C_{n_2}$

Number of microstate for state i th = ${}^{N-n_1-n_2-\dots-n_{i-1}} C_{n_i}$

So, total number of microstate is

$$\begin{aligned} & {}^N C_{n_1} \times {}^{N-n_1} C_{n_2} \times {}^{N-n_1-n_2} C_{n_3} \times \dots \times {}^{N-n_1-n_2-n_3-\dots-n_{i-1}} C_{n_i} \\ &= \frac{N!}{n_1!(N-n_1)!} \times \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \times \dots \times \frac{(N-n_1-n_2-\dots-n_{i-1})!}{n_i!(N-n_1-n_2-\dots-n_i)!} \end{aligned}$$



$$= \frac{N!}{n_1!(N-n_1-n_2-\dots-n_i)!} \quad (\text{For distinguishable particle})$$

$$= \frac{1}{n_1!(N-n_1-n_2-\dots-n_i)!} \quad (\text{For indistinguishable particle})$$

- Q. Four distinguishable coins are tossed a large number of time. Write down the different microstate which may be observed & the macrostate into which they would fall. Give the probability of the most probable macrostate.

Macrostate	Microstate coins having head up	Microstate coins having tail up	No. of microstate	Probability
$n_1 = 4, n_2 = 0$	a b c d	—	1	$\frac{1}{16}$
$n_1 = 3, n_2 = 1$	abc bcd cda dab	d a b c	4	$\frac{4}{16}$
$n_1 = 2, n_2 = 3$	ab ac ad bc bd cd	cd bd bc ad ac ab	6	$\frac{6}{16}$
$n_1 = 1, n_2 = 3$	a b c d	bcd acd abd abc	4	$\frac{4}{16}$
$n_1 = 0, n_2 = 4$	—	abcd	1	$\frac{1}{16}$

Total number of microstate = 16

The probability of most probable state = $6/16$

- Q. An isolated system consist of two non-interacting Spin $\frac{1}{2}$ particles a & b fixed in space & kept in magnetic field B. Find out the total no. of microstates allowed to the system.

Soln.	System state or macrostate	Particle state or Microstate	Magnetic moment	Energy
1		U U	$2\mu_0$	$-2\mu_0 B$
2		U D	0	0
		D U	0	0
3		D D	$-2\mu_0$	$+2\mu_0 B$

Total number of microstates = 4 for spin $\frac{1}{2}$ two particles system.



The number of microstate for N number of spin S as independent, distinguishable and non-interacting particles is

$$\Omega = (2S+1)^N$$

The probability of getting a macrostate in which there are r particles out of N spin $1/2$ particles in spin up state

$$N_{C_r} \times \frac{1}{2^N}$$

Contact Between Statistics and Thermodynamics

Now we consider two physical systems A_1 and A_2 which are separately in equilibrium. Let the macrostate of E_1 be

A_1	A_2
N_1, V_1, E_1	N_2, V_2, E_2

represented by parameter N_1, V_1, E_1 so that it has possible microstate $\Omega_1(N_1, V_1, E_1)$

Similarly system A_2 by parameter N_2, V_2, E_2 so that it has possible microstate $\Omega_2(N_2, V_2, E_2)$

Now bring the two system into contact with each other through a wall (conducting, rigid & impenetrable) such that N_1, N_2 and V_1, V_2 remain fixed but energies E_1 and E_2 become variable such that

$$E_1 + E_2 = E^{(0)} = \text{constant.}$$

The number of microstate at any time t of the composite system is represented by

$$\Omega(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2) = \Omega_1(E_1) \Omega_2(E^{(0)} - E_1) = \Omega(E^{(0)}, E_1)$$

The microstate of composite system is also represented by

$$\Omega(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2) = \Omega_1(E^{(0)} - E_2) \Omega_2(E_2)$$

For maximum number of microstate,

$$\frac{d\Omega}{dE_1} = 0 \Rightarrow \Omega_2 \frac{\partial \Omega_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} = 0 \Rightarrow \Omega_2 \frac{d\Omega_1}{dE_1} - \Omega_1 \frac{d\Omega_2}{dE_2} = 0$$

$$\left\{ \begin{array}{l} \therefore E_2 = E^{(0)} - E_1 \\ \therefore \frac{dE_2}{dE_1} = -1 \end{array} \right.$$

$$\left[\frac{1}{\Omega_1} \left(\frac{\partial \Omega_1}{\partial E_1} \right) \right]_{N_1, V_1, E_1 = \bar{E}_1} = \left[\frac{1}{\Omega_2} \left(\frac{\partial \Omega_2}{\partial E_2} \right) \right]_{N_2, V_2, E_2 = \bar{E}_2} \quad (\because \text{at equilibrium } E_1 \text{ and } E_2 \rightarrow \bar{E})$$

$$\text{Let } \beta = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N, V, E = \bar{E}_1}$$

Under equilibrium $\beta_1 = \beta_2$

$$\frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{N, V} = \frac{1}{k_B T} \quad \text{so} \quad \frac{1}{k_B T_1} = \frac{1}{k_B T_2} \Rightarrow \boxed{T_1 = T_2} \quad \dots (1)$$

This is the condition for thermal equilibrium.

If the wall is movable and conducting

$$\text{Let } \eta = \frac{1}{k_B} \left(\frac{\partial S}{\partial V} \right)_{N, E} = \frac{1}{k_B} \left(\frac{P}{T} \right)$$



Under equilibrium $\eta_1 = \eta_2 \Rightarrow \frac{P_1}{k_B T_1} = \frac{P_2}{k_B T_2}$

For conducting medium $T_1 = T_2 \Rightarrow \boxed{P_1 = P_2}$... (2)

Equation (2) is the condition for mechanical equilibrium and thermal equilibrium.

If the wall is conducting, non-rigid, movable and penetrable

$$V_1 + V_2 = V^0, \quad E_1 + E_2 = E^0, \quad N_1 + N_2 = N^0 \text{ (fixed)}$$

$$\beta_1 = \beta_2 \Rightarrow T_1 = T_2$$

$$\eta_1 = \eta_2 \Rightarrow P_1 = P_2$$

Now, let $\xi = \left(\frac{\partial}{\partial N} \ln \Omega \right)_{E, V}$

$$\frac{1}{k_B} \left(\frac{\partial S}{\partial N} \right)_{E, V} = - \frac{\mu}{k_B T}$$

Under equilibrium,

$$\xi_1 = \xi_2 \Rightarrow \mu_1 = \mu_2 \quad \dots (3)$$

This is the condition for chemical equilibrium.

Moreover, if $T_1 = T_2$, $P_1 = P_2$ and $\mu_1 = \mu_2$ then system is in thermodynamic equilibrium.

Classical ideal gas : Now we discuss the thermodynamical properties of a classical ideal gas composed of N monatomic (non-interacting) molecules by statistical method. The total number of ways in which the N -particle can be distributed in the system will be simply equal to the product of the number of ways in which the individual particles can be distributed in the same space independently of one another volume of phase space.

$$d\tau = \int d^3x d^3p = \int dx dy dz \int d^3p = V \times \frac{4}{3} \pi p^3 \text{ (6D phase space = 3D position and 3D momentum)}$$

where, volume of each phase cell = h^3 (a particle has 3 degree of freedom)

$$\text{So, } \Omega = \text{Number of microstates} = \frac{\text{Volume of phase space}}{\text{Volume of phase cell}} = \frac{V \cdot \frac{4}{3} \pi p^3}{h^3}$$

$$\text{So, } \Omega = \frac{V}{h^3} \frac{\pi p^3}{3/4} = \frac{V}{h^3} \frac{\sqrt{\pi} \pi p^3}{(3/2)!} \Rightarrow \Omega = \frac{V}{h^3} \frac{(2\pi m E)^{3/2}}{\left(\frac{3}{2}\right)!}, \text{ where } p = \sqrt{2mE}$$

Number of microstates composed of N identical particles is

$$\Omega(E) = \left(\frac{V}{h^3} \right)^N \left[\frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2}\right)!} \right] \quad \text{(For sharp energy)}$$

If the energy lies between E and $E + dE$, the number of microstates is



$$\Omega(E + \Delta E) = \Omega(E) + \frac{\partial \Omega}{\partial E} \Delta E \quad \text{where we have neglected higher terms}$$

$$= \left(\frac{V}{h^3} \right)^N \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2} \right)!} \frac{3N}{2} E^{\frac{3N}{2}-1} dE$$

$$\text{Now entropy, } S = k_B \log \Omega = k_B \left[\ln \left(\frac{V}{h^3} \right)^N \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2} \right)!} \right]$$

$$S = k_B \left[\ln \left(\frac{V}{h^3} \right)^N (2\pi m E)^{3N/2} - \ln \left(\frac{3N}{2} \right)! \right]$$

$$= k_B \left[\ln \left(\frac{V}{h^3} \right)^N (2\pi m E)^{3N/2} - \left\{ \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right\} \right] \quad (\log n! = n \log n - n = \text{Stirling's relation})$$

$$S = k_B \left[\ln \left(\frac{V}{h^3} \right)^N (2\pi m E)^{3N/2} - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2} \right] = k_B \left[\ln \left(\frac{V}{h^3} \right)^N (2\pi m E)^{3N/2} - \ln \left(\frac{3N}{2} \right)^{3N/2} + \frac{3N}{2} \right]$$

$$= k_B \left[\ln \left[\left(\frac{V}{h^3} \right)^N \left(\frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2} \right)^{3N/2}} \right) \right] + \frac{3N}{2} \right]$$

$$\boxed{S = N k_B \ln \left[\left(\frac{V}{h^3} \right) \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N k_B} \quad \dots (1)$$

Equation (1) can also be written as

$$S = N k_B \ln \frac{V}{h^3} + N k_B \ln \left(\frac{4\pi m E}{3N} \right)^{3/2} + \frac{3}{2} N k_B$$

$$= N k_B \ln \frac{V}{h^3} + \frac{3}{2} N k_B [1 + \ln (2\pi M k_B T)] \quad \left(\because E = \frac{3}{2} N k_B T \right)$$

$$= N k_B \ln V - N k_B \ln (h^2)^{3/2} + \frac{3}{2} N k_B [1 + \ln (2\pi M k_B T)]$$

$$= N k_B \ln V - \frac{3}{2} N k_B \ln h^2 + \frac{3}{2} N k_B [1 + \ln (2\pi M k_B T)]$$

$$\Rightarrow \boxed{S = N k_B \ln V + \frac{3}{2} N k_B \left[1 + \ln \frac{2\pi M k_B T}{h^2} \right]} \quad \dots (2)$$



From equation (1),

$$E(N, V, S) = \frac{3h^2 N}{4\pi M V^{2/3}} \exp \left[\frac{2S}{3Nk_B} - 1 \right]$$

$$\text{Now, } T = \left(\frac{\partial E}{\partial S} \right)_{N, V} = \frac{3h^2 N}{4\pi M V^{2/3}} \exp \left[\frac{2S}{3Nk_B} - 1 \right] \frac{2}{3Nk_B}$$

$$\Rightarrow T = E \times \frac{2}{3Nk_B} \Rightarrow \boxed{E = \frac{3}{2} Nk_B T}$$

Specific heat :

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} Nk_B$$

Pressure : $TdS = dE + PdV - \mu dN$

$$\Rightarrow P = - \left(\frac{\partial E}{\partial V} \right)_{N, S} = \frac{2}{3} \frac{E}{V} \Rightarrow \boxed{PV = \frac{2}{3} E}$$

$$\text{Now, } PV = \frac{2}{3} \times \frac{3}{2} Nk_B T = Nk_B T$$

$$\Rightarrow \boxed{PV = Nk_B T} \text{ (This is the ideal gas equation.)}$$

$$\text{Now, } C_P = \left(\frac{\partial E + PdV}{\partial T} \right)_P$$

$$\Rightarrow C_P = \left[\frac{\partial}{\partial T} (E + PV) \right]_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$\Rightarrow C_P = \left[\frac{\partial}{\partial T} \left(\frac{3}{2} Nk_B T + Nk_B T \right) \right]_P = \left[\frac{\partial}{\partial T} \left(\frac{5}{2} Nk_B T \right) \right]_P = \frac{5}{2} Nk_B$$

$$\text{Now, } \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2} Nk_B}{\frac{3}{2} Nk_B} = \frac{5}{3}$$

For adiabatic process of an ideal gas, we have

$$PV^\gamma = \text{constant} \Rightarrow PV^{5/3} = \text{constant}$$

Now, we have

$$S = Nk_B \ln \left[\frac{V}{h^3} \left(\frac{4\pi M E}{3N} \right)^{3/2} \right] + \frac{3}{2} Nk_B$$

If we replace, N by αN , V by αV and E by αE , we are not getting αS . So, the above equation of entropy is not showing that S is an extensive property. So, we have to modify it.



Entropy of mixing: The entropy of mixing is defined as

$$\Delta S = S_T - \sum_{i=1}^N S_i, \text{ where } S_T = \text{Total entropy after mixing, } S_i = \text{Entropy before mixing of individual system}$$

Entropy is not an extensive quantity of the system i.e. if we increase the extensive parameter by a factor α , keeping the intensive variable unchanged then the entropy of the system which should also increase by same factor α doesn't increase. The entropy of an ideal gas is not extensive due to the term $\ell n V$. This means that entropy of the system is different from the sum of the entropies of its parts. This is called **Gibbs paradox**. Gibbs visualised the mixing of two ideal gas (1) and (2) both being initially at the same temperature T , the temperature remain same after mixing and before mixing. Now,

$$\begin{aligned} \sum_{i=1}^2 S_i &= \sum_{i=1}^2 N_i k_B \ell n V_i + \frac{3}{2} N_i k_B \left[1 + \ell n \left(\frac{2\pi M_i k_B T}{h^2} \right) \right] \\ &= N_1 k_B \ell n V_1 + \frac{3}{2} N_1 k_B \left[1 + \ell n \left(\frac{2\pi M_1 k_B T}{h^2} \right) \right] + N_2 k_B \ell n V_2 + \frac{3}{2} N_2 k_B \left[1 + \ell n \left(\frac{2\pi M_2 k_B T}{h^2} \right) \right] \end{aligned}$$

Now, the total entropy after mixing is

$$S_T = (N_1 + N_2) k_B \ell n (V_1 + V_2) + \frac{3}{2} (N_1 + N_2) k_B \left[1 + \ell n \left(\frac{2\pi M k_B T}{h^2} \right) \right]$$

where, $N = N_1 + N_2$ and $V = V_1 + V_2$

Here, $M_1 = M_2 = M$

So, the entropy of mixing is

$$\begin{aligned} \Delta S &= S_T - \sum_{i=1}^2 S_i = (N_1 + N_2) k_B \ell n (V_1 + V_2) + \frac{3}{2} (N_1 + N_2) k_B \left[1 + \ell n \left(\frac{2\pi M k_B T}{h^2} \right) \right] \\ &\quad - N_1 k_B \ell n V_1 - \frac{3}{2} N_1 k_B \left[1 + \ell n \left(\frac{2\pi M k_B T}{h^2} \right) \right] - N_2 k_B \ell n V_2 - \frac{3}{2} N_2 k_B \left[1 + \ell n \left(\frac{2\pi M k_B T}{h^2} \right) \right] \\ &= (N_1 + N_2) k_B \ell n (V_1 + V_2) - N_1 k_B \ell n V_1 - N_2 k_B \ell n V_2 \\ &= [N_1 k_B \ell n (V_1 + V_2) - N_1 k_B \ell n V_1] + [N_2 k_B \ell n (V_1 + V_2) - N_2 k_B \ell n V_2] \\ &\Rightarrow \boxed{\Delta S = N_1 k_B \ell n \frac{V_1 + V_2}{V_1} + N_2 k_B \ell n \frac{V_1 + V_2}{V_2}} \end{aligned}$$

Since $\frac{V_1 + V_2}{V_1} > 1$ and $\frac{V_1 + V_2}{V_2} > 1$, So $\Delta S > 0$

If initial density of the gases is equal to the density of mixture i.e., $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}$, we have

$$\Delta S = k_B \left[N_1 \ell n \frac{N_1 + N_2}{N_1} + N_2 \ell n \frac{N_1 + N_2}{N_2} \right]$$

$$\Delta S > 0$$



So, if we consider the mixing of two same gas with a common initial temperature T and a common initial particle density (reversible process), we are getting

$$\Delta S > 0$$

But for reversible process, we should get $\Delta S = 0$

Thus once again we are led to believe that there is something basically wrong with that expression. To avoid the paradoxical situation Gibbs diminished entropy(S) by an another term $k_B \ell n N!$ i.e., S_1 by $k_B \ell n N_1!$ and S_2 by $k_B \ell n N_2!$. So, we have

$$\begin{aligned} S &= Nk_B \ell n V + \frac{3}{2} Nk_B \left[1 + \ell n \left(\frac{2\pi mk_B T}{h^2} \right) \right] - k_B \ell n N! \\ &= Nk_B \ell n V + \frac{3}{2} Nk_B \left[1 + \ell n \left(\frac{2\pi mk_B T}{h^2} \right) \right] - Nk_B \ell n N + Nk_B \end{aligned}$$

$$S = Nk_B \ell n \frac{V}{N} + \frac{3}{2} Nk_B \left[\frac{5}{2} + \ell n \left(\frac{2\pi mk_B T}{h^2} \right) \right]$$

This is known as Sackur Tetrode equation.

Now, if we replace E by αE , V by αV and N by αN , we are getting αS . So, S is an extensity property.

Chemical Potential :

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V,S} = E \left[\frac{S}{3N} - \frac{2S}{3N^2 k_B} \right] = k_B T \ell n \left(\frac{N}{V} \left(\frac{h^2}{2\pi mk_B T} \right)^{3/2} \right)$$

Gibb's free energy :

$$G = \mu N = Nk_B T \ell n \left[\frac{N}{V} \left(\frac{h^2}{2\pi mk_B T} \right)^{3/2} \right]$$

Helmholtz free energy :

$$\text{So, } A = E - TS = Nk_B T \left[\ell n \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi mk_B T} \right)^{3/2} \right\} - 1 \right]$$

Here, A is an extensive property while μ is an intensive property of the system.

- Q.** We have equal amount of two identical ideal gases at the same temperature T but at different pressure P_1 and P_2 in two containers of volume V_1 and V_2 respectively. The containers are connected. Find the change in entropy (The temperature after mixing also remains same)

Soln. We know that, $S = Nk_B \ell n \left(\frac{V}{N} \right) + \frac{3}{2} Nk_B \left[\frac{5}{2} + \ell n \left(\frac{2\pi mk_B T}{h^2} \right) \right]$

So, the entropy before mixing is

$$\sum_{i=1}^2 S_i = N_1 k_B \ell n \frac{V_1}{N} + \frac{3}{2} N_1 k_B \left[\frac{5}{2} + \ell n \left(\frac{2\pi mk_B T}{h^2} \right) \right]$$



$$= Nk_B \ln \frac{V_1}{N} + \frac{3}{2} Nk_B \left[\frac{5}{2} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] + Nk_B \ln \frac{V_2}{N} + \frac{3}{2} Nk_B \left[\frac{5}{2} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Using $PV = Nk_B T \Rightarrow \frac{V}{N} = \frac{k_B T}{P}$, we have

$$\sum_{i=1}^2 S_i = Nk_B \ln \frac{k_B T}{P_1} + \frac{3}{2} Nk_B \left[\frac{5}{2} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] + Nk_B \ln \frac{k_B T}{P_2} + \frac{3}{2} Nk_B \left[\frac{5}{2} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

The total entropy after mixing is

$$S_T = 2Nk_B \ln \frac{V_1 + V_2}{2N} + \frac{3}{2} \times 2Nk_B \left[\frac{5}{2} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

The change in entropy after mixing is

$$\Delta S = S_T - \sum_{i=1}^2 S_i = 2Nk_B \ln \frac{V_1 + V_2}{2N} - Nk_B \ln \frac{k_B T}{P_1} - Nk_B \ln \frac{k_B T}{P_2} = Nk_B \ln \frac{\left(\frac{k_B T}{P} \right)^2}{\left(\frac{k_B T}{P_1} \right) \left(\frac{k_B T}{P_2} \right)}$$

Now, we have

$$P(V_1 + V_2) = 2Nk_B T \Rightarrow \frac{1}{P} = \frac{V_1 + V_2}{2Nk_B T} = \frac{V_1}{2Nk_B T} + \frac{V_2}{2Nk_B T} = \frac{1}{2} \left(\frac{1}{P_1} + \frac{1}{P_2} \right)$$

$$\Delta S = Nk_B \ln \left[\frac{(k_B T)^2 (P_1 + P_2)^2}{(2 P_1 P_2)^2} \times \frac{P_1 P_2}{(k_B T)^2} \right] \Rightarrow \Delta S = Nk_B \ln \frac{(P_1 + P_2)^2}{4 P_1 P_2}$$

Here we get $\Delta S > 0$

(We are considering identical particle. So it is a reversible case only when the particle density is same otherwise for identical gas, we will also get $\Delta S > 0$).

Phase Space

Phase Space: $d\tau = dx dy dz dP_x dP_y dP_z$

$$= dx dP_x dy dP_y dz dP_z = h \cdot h \cdot h = h^3$$

Volume of phase cell $= h^{3N} = h^f$

Dimension of phase space $= 2f$ (f degree of freedom). If f is the degree of freedom of a single particle and N is the total no. of particle, then dimension of phase space is $= 2Nf$

No. of microstate in phase space $= \frac{\text{Total Volume of Phase Space allowed to the system}}{\text{Volume of phase Cell } (h^3)}$

Q. Calculate the number of microstate for a free particle in 3-dimension that have momentum p .

Solu. $d\tau = dx dy dz dp_x dp_y dp_z$

Allowed Phase Space Volume $= \int d\tau = \int dx dy dz \int dp_x dp_y dp_z$

$$= V \int p^2 dp \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = V \frac{4}{3} \pi p^3$$



$$\text{No. of microstate} = \frac{V}{h^3} \times \frac{4}{3} \pi p^3$$

Note : for 2-D,

$$\int dt = \int dx \int dy \int dp_x \int dp_y = \int d^2q \cdot d^2p = A \cdot \pi p^2 \quad \{\text{where } A = \text{area}\}$$

If momentum lies between p and $p + dp$,

$$\text{Therefore, number of microstate} = \frac{2A}{h^2} 2\pi p dp = \frac{4\pi A}{h^2} p dp$$

Phase Space Diagram of an Oscillator

Energy of a one dimensional harmonic oscillator whose position co-ordinate is x and momentum co-ordinate is P_x is given by

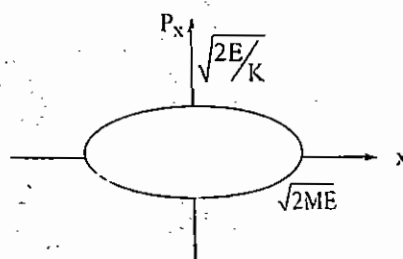
$$E = \frac{P_x^2}{2m} + \frac{1}{2} Kx^2 \quad \text{where, } K = m\omega^2 \quad \text{and } \omega = \text{angular frequency}$$

where the 1st term is the K.E and the 2nd term is P.E. What is the trajectory of oscillator in phase space?

Q. Find the accessible region & the no. of accessible microstate of oscillator?

$$\text{Soln. } E = \frac{P_x^2}{2m} + \frac{1}{2} Kx^2 \quad \text{or} \quad \frac{P_x^2}{2mE} + \frac{Kx^2}{2E} = 1$$

$$\Rightarrow \frac{P_x^2}{(\sqrt{2mE})^2} + \frac{x^2}{\left(\sqrt{\frac{2E}{K}}\right)^2} = 1$$



For constant energy E , equation (1) describes an ellipse in phase space i.e. $x - P_x$ plane.

The phase points are those lying on the elliptical path having a semimajor axis $\sqrt{2mE}$ and semiminor axis $\sqrt{\frac{2E}{K}}$.

At any particular instant the phase space of the oscillator is represented by some point on the ellipse.

The area of the ellipse in phase space is πab where a is the semimajor axis and b is the semiminor axis. So,

$$A = \pi ab = \pi \sqrt{2mE} \sqrt{\frac{2E}{K}} = 2\pi E \sqrt{\frac{m}{K}} = \frac{2\pi E}{\omega}$$

It represents the phase space available to the oscillator having energy between 0 and E or this is the accessible region.

$$\text{Now the accessible no. of microstates} = \frac{\text{Area of accessible region}}{\text{Area of a point in phase space (i.e. cell)}} = \frac{2\pi E}{\omega h} = \frac{E}{\omega \hbar}$$

The phase space available to the oscillator having energy between E and $E + dE$ is

$$dA = 2\pi \sqrt{\frac{m}{K}} dE = \frac{2\pi}{\omega} dE$$



Q. Calculate the number of microstates accessible to the photon having frequency between ν and $\nu + d\nu$ confined to a 3 dimensional cavity of volume V .

Soln. Number of microstates in frequency range 0 to ν is

$$\Omega = \frac{V}{h^3} \frac{4}{3} \pi p^3 = \frac{V}{h^3} \frac{4}{3} \pi \left(\frac{h\nu}{c} \right)^3 = \frac{4}{3} \frac{\pi V \nu^3}{c^3} \text{ where, we have used } p = \frac{E}{c} = \frac{h\nu}{c}$$

Number of microstates in the frequency range ν and $\nu + d\nu$ is

$$\therefore g(\nu) = \frac{8\pi V}{c^3} \nu^2$$

The density of state is

$$\therefore g(\nu) = \frac{8\pi V}{c^3} \nu^2$$

Moreover, each photon has two polarization states. So, the density of state must be multiplied by factor of 2.

PREVIOUS YEARS SOLUTIONS OF JEST

Q. Suppose that the number of microstates available to a system of N particles depends on N and the combined variable UV^2 , where U is the internal energy and V is the volume of the system. The system initially has volume 2m^3 and energy 200 J . It undergoes an isentropic expansion to volume 4m^3 . What is the final pressure of the system in SI units? **[JEST 2017]**

Soln. Given : $\Omega = cUV^2$, where c is a proportionality constant.

$$\text{Now, } S = k_B \ln \Omega = k_B \ln (cUV^2)$$

$$\therefore dS = k_B \frac{dU}{U} + 2k_B \frac{dV}{V}$$

Comparing this with combined I and II law of thermodynamics

$$dS = \frac{dU}{T} + \frac{P}{T} dV, \text{ we have}$$

$$U = k_B T \text{ and } P = \frac{2k_B T}{V}$$

$$\therefore P = \frac{2U}{V} = 2 \times \frac{200}{2} = 200 \text{ N/m}^2.$$

Correct answer is (200)

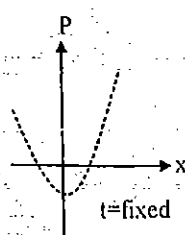
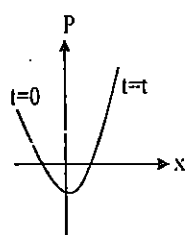
Chapter 6

Ensembles in Statistical Physics

The description of any system in statistical physics is done by considering ensembles. Once we know our ensemble (collection of systems etc.), we can quickly apply the laws of statistical mechanics to it and understand the physics thereof.

Part of phase line constructed due to the motion of phase point with time. Each phase point on the line corresponds to different time co-ordinates.

Gibbs replace this time dependent picture by a static picture (time fix) in which the entire phase line exists at one time. Then each phase point represents a separate system that are macroscopically identical but microscopically different to the system of interest. These systems are non-interacting independent system. All members are identical in features like N, V, E . (macrostate) but differing position and momenta co-ordinates of individual molecules (microscopically)



A collection of large no. of independent systems which are macroscopically identical but microscopically different is called ensemble.

The concept of ensemble helps in understanding the actual system more completely. It represents at one time the microstate of actual system which would occur in the course of time. We study the statistical behaviour of the ensemble by the knowledge of the behaviour of the ensemble we can predict the probable behaviour of the system under consideration.

1. **Microcanonical ensemble (N, V, E)** : The ensemble in which all element have same macrostate represented by same no. of particle N , same volume V and same energy E i.e. macrostate is specified by (N, V, E) for all elements (systems). All elements of microcanonical ensemble are separated by impenetrable, rigid and non-interacting walls such that values of (N, V, E) for a particular system are not affected by the presence of other system i.e. all systems are isolated to each other.
2. **Canonical ensemble (N, V, T)** : The ensemble in which all elements will have same macrostate represent by same N, V, T for all elements. The elements of a canonical ensemble are separated from each other by impenetrable, rigid and conducting walls such that the values of N, V, T for a particular system are not affected by others. In canonical ensemble, each element is in thermal contact (equilibrium) with heat reservoir or with all other elements of the ensemble at temperature T . In this ensemble elements can exchange energy but not particles.



3. **Grand canonical ensemble** (μ, V, T): The ensemble in which all elements will have same macrostate represented by same μ, V, T for all elements. The elements of a grand canonical ensemble are separated from each other by penetrable, rigid and conducting walls such that the values of μ, V, T for a particular system aren't affected by others. In this ensemble the elements are in contact with particle energy reservoir. The elements can exchange energy as well as particles.

Microcanonical Ensemble

Microcanonical ensemble: For microcanonical ensemble, energy remains constant (systems are isolated)

Density Function ρ : The density function gives the idea of number of representative points lying in the region allowed to the system.

$$\rho(q, p) = \rho(E) = \text{constant} \quad (\text{for sharp value of energy})$$

We may prefer to specify a range of energy value $\left(E - \frac{1}{2}\Delta\right)$ to $\left(E + \frac{1}{2}\Delta\right)$ rather than a sharply defined value of E . Accordingly the representative points of the ensemble have a choice to lie anywhere within a hypershell defined by the condition.

$$\rho(q, p) = \begin{cases} \text{constant if} & E - \frac{1}{2}\Delta < H(p, q) < E + \frac{1}{2}\Delta \\ 0 & \text{Otherwise} \end{cases}$$

Accordingly the expectation value of any variable $f(q, p)$ is given by

$$\langle f(q, p) \rangle = \frac{\int f(q, p) \rho(q, p) d\omega}{\int \rho(q, p) d\omega}$$

where, $d\omega = d^{3N}q d^{3N}p$ = volume element in phase space

Since $\rho(q, p)$ is constant, we have

$$\langle f(q, p) \rangle = \frac{\int f(q, p) d\omega}{\int d\omega}$$

The expectation value of representative points lying in a volume element $d\omega$ of the relevant hypershell is simply proportional to volume element $d\omega$. In other words, a prior probability of finding a representative point in a given volume element is equal to the probability of finding a representative point in an equivalent volume element $d\omega$ located anywhere in the hypershell. This is the postulate of equal a prior probability of representative points or microstate.

Stationary ensemble :

1. The ensemble for which density function is constant is called stationary ensemble (microcanonical).
2. If $\frac{\partial \rho}{\partial t} = 0$ for an ensemble then that ensemble is called stationary ensemble (microcanonical).

Ensemble average of any physical quantity is identical with the value on except to obtain on making an appropriate measurement on the given system.

The thermodynamics of the system in microcanonical ensemble would then be discussed by calculating the no. of microstate in accessible regions

$$\Omega = \frac{\text{Volume of accessible region in phase space}}{\text{Volume of phase cell}}$$

$$\Omega = \frac{w}{w_0} \quad \text{where, } w_0 = h^f \text{ and } f \text{ is the degree of freedom}$$



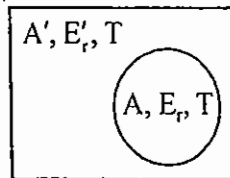
Canonical Ensemble

In canonical ensemble, the energy E of a system become variable and can take values from 0 to ∞ .

Equilibrium between a system and a heat reservoir :

We consider the given system A , immersed in a very large heat reservoir A' . In the equilibrium both the system and the heat reservoir would have the common temp T . Their energies however would be variable and could have, at any time t , values lying anywhere between 0 and E^0

[E = energy of A (E_r) + energy of A' (E'_r)]. If at any particular instant of time, the system A happens to be in a state characterised by the energy E_r , then the reservoir would have energy E'_r .



such that, $E_r + E'_r = E^0 = \text{constant}$

Since the reservoir is much larger than the given system, $E_r \ll E^0$

$$\text{and hence, } \frac{E_r}{E^0} = \frac{E^0 - E'_r}{E^0} = \left(1 - \frac{E'_r}{E^0}\right) \ll 1$$

With the state of the system with energy E_r , the reservoir can still be in any one of the large number of states compatible with the energy E'_r . Let the no. of states be denoted by $\Omega'(E'_r)$. The larger the number of states available to the reservoir, the larger probability of the reservoir assuming that particular energy value E'_r . Since the various possible states are equally likely to occur, the relevant probability would be directly proportional to this number. So, we have

$$P_r \propto \Omega'(E'_r) \equiv \Omega'(E^{(0)} - E_r)$$

$$P_r = C \Omega'(E^{(0)} - E_r) \Rightarrow \ln P_r = \ln \Omega'(E^{(0)} - E_r) + \ln C = \ln \Omega'(E_r + E^{(0)} - E^{(0)}) + \ln C$$

Expanding the series about $E_r = 0$ and $E'_r = E^{(0)}$ using Taylor's series expansion, we have

$$\ln P_r = \ln \Omega'(E'_r) \Big|_{E'_r = E^{(0)}} + (E'_r - E^{(0)}) \frac{\partial}{\partial E'_r} \ln \Omega'(E'_r) \Big|_{E'_r = E^{(0)}} + \ln C$$

$$\Rightarrow \ln P_r = \ln K' + (-E_r) \frac{\partial}{\partial E'_r} \ln \Omega'(E'_r) \Big|_{E'_r = E^{(0)}} + \ln C, \text{ where } K' = \Omega'(E^{(0)})$$

Taking $\ln K + \ln C = \ln K'$, we have

$$\ln P_r = \ln K + (-E_r) \frac{\partial}{\partial E'_r} \ln \Omega'(E'_r) \Big|_{E'_r = E^{(0)}}$$

$$\Rightarrow \ln P_r = \ln K - \beta E_r$$

$$\Rightarrow P_r = K e^{-\beta E_r}$$

$$\text{Using } \sum_r P_r = 1, \text{ we have } K = \frac{1}{\sum_r \exp(-\beta E_r)}. \text{ So,}$$

Q.

Soln.



$$P_i = \frac{e^{-\beta E_i}}{\sum_r e^{-\beta E_r}}$$

If the level have multiplicity or degeneracy or statistical weight g_r , then

$$P_r = \frac{g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}$$

where the denominator represents the partition function. So,
Partition function for quantum mechanical system (discrete energy)

$$Q_N(V, T) = \sum_r g_r e^{-\beta E_r}$$

Partition function for classical distinguishable system is

$$Q_N(V, T) = \frac{1}{h^{3N}} \int e^{-\beta E_r} d^3p d^3q$$

Partition function for semiclassical indistinguishable system is

$$Q_N(V, T) = \frac{1}{h^{3N}} \frac{1}{N!} \int e^{-\beta E_r} d^3p d^3q$$

$$Q_N(V, T) = [Q_1(V, T)]^N \quad \text{distinguishable}$$

$$= \frac{[Q_1(V, T)]^N}{N!} \quad \text{indistinguishable}$$

The partition function indicates that how the particles are partitioned among the various energy states of the system

Q. Show that the partition function of two independent (non-interacting) system i and j is given by

$$Z_{ij} = Z_i \times Z_j$$

Soln. We know that

$$P_i = \frac{e^{-\beta E_i}}{Z_i} \quad \text{and} \quad P_j = \frac{e^{-\beta E_j}}{Z_j} \quad \text{where for the combined system, we have}$$

$$E = E_i + E_j \quad \text{and hence,} \quad P_{ij} = \frac{e^{-\beta(E_i + E_j)}}{Z_{ij}}$$

$$\text{Now, } P_{ij} = \frac{e^{-\beta E}}{Z_{ij}} = \frac{e^{-\beta(E_i + E_j)}}{Z_{ij}} = \frac{e^{-\beta E_i} \times e^{-\beta E_j}}{Z_{ij}}$$

Using $P_{ij} = P_i \times P_j$, we have

$$\frac{e^{-\beta E_i} \times e^{-\beta E_j}}{Z_{ij}} = \frac{e^{-\beta E_i}}{Z_i} \times \frac{e^{-\beta E_j}}{Z_j}$$

$$\text{So } Z_{ij} = Z_i \times Z_j$$



In general $Z_{ijk...} = Z_i \times Z_j \times Z_k \times \dots$

For example, total partition function of a diatomic molecule having all rotational, translational and vibrational energy is

$$Z = Z_{\text{Rotational motion}} \times Z_{\text{Translational motion}} \times Z_{\text{Vibrational motion}} \times \dots$$

- Q.** A system consist of three independent particles localised in space. Each particle have two states of energy 0 and E. When the system is in thermal equilibrium with a heat bath at temperature T. Calculate its partition function ?

Soln. Method: 1

$$Q_N(V, T) = \sum_r g_r e^{-\beta E_r}$$

$$Q_1(V, T) = \sum e^{-\beta E_r} = 1 + e^{-\beta E} \quad (\text{put } E_r = 0 \text{ \& } E)$$

$$Q_3(V, T) = [Q_1(V, T)]^3 = (1 + e^{-\beta E})^3 = 1 + e^{-3\beta E} + 3e^{-2\beta E} + 3e^{-\beta E}$$

Method: 2

Macrostate	Energy State (Microstate)		Total Energy	Degeneracy
	0	E		
1	abc		0	$g_1 = 1$
2	ab	c	E	$g_2 = 3$
	bc	a	E	
	ca	b	E	
3	a	bc	2E	$g_3 = 3$
	b	ac	2E	
	c	ab	2E	
4	abc		3E	$g_4 = 1$

$$Q_N(V, T) = \sum_r g_r e^{-\beta E_r}$$

$$= g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} + g_4 e^{-\beta E_4} = 1 + 3e^{-\beta E} + 3e^{-2\beta E} + e^{-3\beta E}$$

- Q.** The partition function for two Bose particle each of which can occupy any of the energy level 0 and E

i) $1 + e^{-2E/KT} + 2e^{-E/KT}$

ii) $1 + e^{-2E/KT} + e^{-E/KT}$

iii) $2e^{-2E/KT} + e^{-E/KT}$

iv) $e^{-2E/KT} + e^{-E/KT}$

Soln.

	0	E	Total energy	degeneracy
1	aa	0	0	1 (g_1)
2	a	a	E	1 (g_2)
3	0	a	2E	1 (g_3)

$$Q_N(V, T) = \sum_r g_r e^{-\beta E_r} = g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} = 1 + e^{-\beta E} + e^{-2\beta E}$$

Correct option is (ii)



Q. The partition function of single gas molecule is Z_α . The partition function of N such non-interacting gas molecule is given by

(i) $\frac{(Z_\alpha)^N}{N!}$

(ii) $(Z_\alpha)^N$

(iii) $N Z_\alpha$

(iv) $(Z_\alpha)^N / N$

Soln. The gas molecule are indistinguishable particles and hence, $Z_N = \frac{(Z_\alpha)^N}{N!}$

Correct option is (i)

Q. A system has energy level $E_0, 2E_0, 3E_0, \dots$ where the excited state are triply degenerate. Four non-interacting Bosons are placed in this system. If the total energy of these Bosons is $5E_0$. The number of microstate is

(i) 2

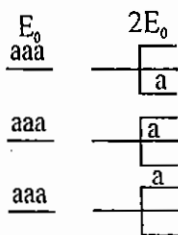
(ii) 3

(iii) 4

(iv) 5

Soln. Total energy = $5E_0$

For this 3 bosons must be in E_0 state and 1 in $2E_0$ state.



Correct option is (ii)

Q. An ensemble of quantum harmonic oscillator is kept at a finite temperature T where,

$$T = \frac{1}{k_B \beta}, \quad k_B \text{ is the Boltzmann constant}$$

The partition function of a single oscillator with energy $(n + \frac{1}{2})\hbar\omega$ is given by

(i) $Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$

(ii) $Z = \frac{e^{-\beta\hbar\omega/2}}{1 + e^{-\beta\hbar\omega}}$

(iii) $Z = \frac{1}{1 - e^{-\beta\hbar\omega}}$

(iv) $Z = \frac{1}{1 + e^{-\beta\hbar\omega}}$

Soln. (i) $Q_1(V, T) = \sum_r e^{-\beta E} = \sum_n e^{-\beta(n + \frac{1}{2})\hbar\omega} = e^{-\beta\hbar\omega/2} + e^{-\frac{3}{2}\beta\hbar\omega} + e^{-\frac{5}{2}\beta\hbar\omega} + \dots$

$$= e^{-\beta\hbar\omega/2} (1 + e^{-\beta\hbar\omega} + e^{-\beta\hbar\omega} + \dots) = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right) \quad \left(\because \sum_{n=0}^{\infty} (r)^n = \frac{1}{1-r}, \text{ for } r < 1 \right)$$

Correct option is (i)



Q. The average number of energy quanta of the oscillator is given by

$$(i) \langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \quad (ii) \langle n \rangle = \frac{e^{-\beta \hbar \omega}}{e^{\beta \hbar \omega} - 1}$$

$$(iii) \langle n \rangle = \frac{1}{e^{\beta \hbar \omega} + 1} \quad (iv) \langle n \rangle = \frac{e^{-\beta \hbar \omega}}{e^{\beta \hbar \omega} + 1}$$

Soln. (i) The average energy of a quantum oscillator is given by

$$U = N \left[\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]$$

If we neglect the zero point energy the average energy become

$$U = \frac{N \hbar \omega}{e^{\beta \hbar \omega} - 1}$$

$$\text{Average number of energy quanta} = \frac{U}{N \hbar \omega} = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Correct option is (i)

Q. In a particular salt among N -atoms each atom has a spin $1/2$ and is associated with a magnetic dipole moment μ_B . The distance between the magnetic atoms is large enough to make the interaction between them negligible. In other words our system is an idealised spin system. The salt is placed in an external magnetic field B . Find the partition function of the individual atom and that for the salt

Soln. $Q_1(V, T) = \sum_r e^{-\beta E_r}$, where $E = \begin{cases} -\mu_B B & \text{for } S = \frac{1}{2} \\ \mu_B B & \text{for } S = -\frac{1}{2} \end{cases} = e^{-\beta \mu_B B} + e^{\beta \mu_B B}$

Since the salt consist of N number of distinguishable particles, we have

$$Q_N(V, T) = [Q_1(V, T)]^N = [e^{-\beta \mu_B B} + e^{\beta \mu_B B}]^N$$

Q. Consider a system of two identical particles which may occupy any of the three levels $0, \epsilon$ and 2ϵ . The lowest energy state is doubly degenerates. The system is in thermal equilibrium at temperature T . Determine the partition function and average energy of the system if particles obey

(i) M-B statistics (ii) B-E statistics (iii) F-D statistics.

Soln: (i) For M-B statistics:

$$Q_N(V, T) = \sum g_r e^{-\beta E_r} = 4 + 4e^{-\beta \epsilon} + 5e^{-2\beta \epsilon} + 2e^{-3\beta \epsilon} + e^{-4\beta \epsilon}$$

$$\text{So, } \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N(V, T) = \frac{\epsilon [4e^{-\beta \epsilon} + 10e^{-2\beta \epsilon} + 6e^{-3\beta \epsilon} + 4e^{-4\beta \epsilon}]}{Q_N(V, T)}$$

(ii) For B-E statistics:

$$Q_N(V, T) = 1 + e^{-\beta \epsilon} + 3e^{-2\beta \epsilon} + e^{-3\beta \epsilon} + e^{-4\beta \epsilon}$$

$$\text{So, } \langle E \rangle = \frac{\epsilon [2e^{-\beta \epsilon} + 6e^{-2\beta \epsilon} + 3e^{-3\beta \epsilon} + 4e^{-4\beta \epsilon}]}{Q_N(V, T)}$$



(iii) For F-D statistics:

$$Q_N(V, T) = 1 + 2e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

$$\text{So, } \langle E \rangle = \frac{\epsilon(2e^{-\beta\epsilon} + 4e^{-2\beta\epsilon} + 3e^{-3\beta\epsilon})}{Q_N(V, T)}$$

Thermodynamical Quantities in Canonical Ensemble

(Physical significance of various statistical quantities in canonical ensemble)

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

where U & β can be determined by the eqn.

$$\begin{aligned} \text{Internal energy or average energy, } U = \langle E_r \rangle &= \sum_r E_r P_r = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \ln \sum_r e^{-\beta E_r} \\ &= -\frac{\partial}{\partial \beta} \ln Q_N(V, T) \quad \dots (1) \end{aligned}$$

Helmholtz free energy :

$$A = U - TS$$

$$\therefore dA = dU - TdS - SdT$$

$$= TdS - PdV + \mu dN - TdS - SdT \quad \text{where, } dQ = TdS = PdV - \mu dN + dU$$

$$= -PdV - SdT + \mu dN$$

$P = -\left(\frac{\partial A}{\partial V}\right)_{T, N}$	$S = -\left(\frac{\partial A}{\partial T}\right)_{V, N}$	$\mu = \left(\frac{\partial A}{\partial N}\right)_{V, T}$
Pressure	entropy	chemical potential

$$\therefore U = A + TS$$

$$= A - T \left(\frac{\partial A}{\partial T} \right)_{N, V}$$

$$U = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_{N, V}$$

$$U = \frac{\partial \left(\frac{A}{T} \right)}{\partial \left(\frac{1}{T} \right)}_{N, V} = \frac{\partial \left(\frac{A}{k_B T} \right)}{\partial \left(\frac{1}{k_B T} \right)}_{N, V}$$

$$U = \left[\frac{\partial}{\partial \beta} \left(\frac{A}{k_B T} \right) \right]_{N, V} \quad \dots (2)$$



Comparing eqn (1) and (2)

$$\frac{A}{k_B T} = -\ln Q_N(V, T)$$

$$A = -k_B T \ln Q_N(V, T)$$

A is an extensive (additive) property

Molar specific heat (C_V):

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} = \left[\frac{\partial}{\partial T} (A + TS) \right]_{N,V} = \left[\frac{\partial}{\partial T} \left[A - T \left(\frac{\partial A}{\partial T} \right)_{N,V} \right] \right]_{N,V}$$

$$= \left(\frac{\partial A}{\partial T} \right)_{N,V} - \left(\frac{\partial A}{\partial T} \right)_{N,V} - T \left[\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial T} \right)_{N,V} \right]_{N,V}$$

$$C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_{N,V}$$

Gibb's free Energy :

$$G = A + PV = A - V \left(\frac{\partial A}{\partial V} \right)_{N,T} \quad \dots (3)$$

Taking, $A = A(N, V, T)$, we have

$$dA = \left(\frac{\partial A}{\partial N} \right)_{V,T} dN + \left(\frac{\partial A}{\partial V} \right)_{N,T} dV = \mu dN - PdV \quad (\because \text{since } T = \text{constant})$$

Integrating keeping intensive variable constant

$$A = \mu N - PV = \left(\frac{\partial A}{\partial N} \right)_{V,T} N + \left(\frac{\partial A}{\partial V} \right)_{N,T} V$$

Putting this value in above equation (3),

$$\begin{aligned} G = A + PV &= A - V \left(\frac{\partial A}{\partial V} \right)_{N,T} = \left(\frac{\partial A}{\partial N} \right)_{V,T} N + \left(\frac{\partial A}{\partial V} \right)_{N,T} V - V \left(\frac{\partial A}{\partial V} \right)_{N,T} \\ &= N \left(\frac{\partial A}{\partial N} \right)_{V,T} = N\mu \Rightarrow \boxed{G = N\mu} \end{aligned}$$

Entropy: $P_r = Q_N^{-1} e^{-\beta E_r}$

$$\ln P_r = \ln (Q_N^{-1} e^{-\beta E_r}) = \ln Q_N^{-1} + \ln e^{-\beta E_r} = -\ln Q_N - \beta E_r$$

$$\langle \ln P_r \rangle = -\ln Q_N - \beta \langle E_r \rangle = \frac{A}{k_B T} - \beta U = \beta (A - U) = -\beta TS = -\frac{S}{k_B}$$

$$\Rightarrow S = -k_B \langle \ln P_r \rangle$$

$$\Rightarrow \boxed{S = -\sum_r P_r \ln P_r} \quad \dots (4)$$

If $T = 0$ i.e system is in ground state and we know ground state is unique then



$$P_r = 1 \quad \text{for ground state} \\ = 0 \quad \text{for all other state}$$

$$S = -(k_B P_0 \ln P_0 + k_B P_1 \ln P_1 + \dots) = \ln 1 = 0 \\ = k_B \times 0 = 0$$

This is the third law of thermodynamics. We also infer that vanishing entropy and perfect statistical order which implies (complete predictability about the system) go together

Largeness of entropy & high degree of statistical disorder (unpredictability) in the system also go together.

Equation (4) also apply in the microcanonical ensemble for each member of system of the ensemble, we have

a group of Ω state which are all equally likely to occur. The value of P_r is less than $\frac{1}{\Omega}$ for each of these states and 0 for all other states. So,

$$S = -k_B \sum_{r=1}^{\Omega} \left\{ \frac{1}{\Omega} \left(\ln \frac{1}{\Omega} \right) \right\} = k_B \ln \Omega$$

Thermodynamics of classical ideal gas using Canonical Ensemble :

Now we consider an ideal gas consisting of n - molecules (non-interacting). we consider the gas molecule indistinguishable

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(q, p)} d^{3N} q d^{3N} p \quad \text{where, } H = \frac{p^2}{2m} \text{ for classical ideal gas molecules.}$$

$$\therefore Q_1(V, T) = \frac{1}{h^3} \int_0^\infty e^{-\frac{\beta p^2}{2m}} d^3 q d^3 p$$

$$Q_1(V, T) = \frac{V}{h^3} \int_0^\infty e^{-\frac{\beta p^2}{2m}} 4\pi p^2 dp \quad \left\{ \int d^3 q = V \right\}$$

But we know that

$$\int_0^\infty e^{-ax^2} x^n dx = \frac{1}{2} a^{-\frac{(n+1)}{2}} \Gamma\left(\frac{n+1}{2}\right)$$

$$\therefore Q_1(V, T) = \frac{V}{h^3} 4\pi \times \frac{1}{2} \left(\frac{\beta}{2m}\right)^{-\frac{3}{2}} \Gamma\left(\frac{3}{2}\right) = \frac{V}{h^3} \times 4\pi \times \frac{1}{2} \left(\frac{2m}{\beta}\right)^{\frac{3}{2}} \frac{1}{2} \sqrt{\pi} \left\{ \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \right\}$$

$$\therefore Q_N(V, T) = \frac{(Q_1(V, T))^N}{N!} = \frac{V^N}{h^{3N} N!} (2\pi m k_B T)^{\frac{3N}{2}}$$

where, $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the mean thermal wavelength

So, $Q_1(V, T) = \frac{V}{\lambda^3}$ for single particle partition function

$$\text{And hence, } Q_N(V, T) = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

$$\Rightarrow \ln Q_N(V, T) = \ln \left(\frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \right) = \ln \left(\frac{V}{\lambda^3} \right)^N - \ln N!$$

$$= N \ln \left(\frac{V}{\lambda^3} \right) - N \log N + N = N \ln \left(\frac{V}{N \lambda^3} \right) + N$$



Helmholtz free Energy (A) :

$$A = -k_B T \ln Q_N(V, T)$$

$$= -k_B T \left[N \ln \left(\frac{V}{N \lambda^3} \right) + N \right] = N k_B T \left[\ln \left(\frac{N \lambda^3}{V} \right) - 1 \right] = N k_B T \left[\ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right) - 1 \right]$$

Chemical potential :

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T, V} = \left[\frac{\partial}{\partial N} \left[N k_B T \left(\ln \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} - 1 \right) \right] \right]_{T, V} = k_B T \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\}$$

Pressure : $P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = - N k_B T \left(- \frac{1}{V} \right) = \frac{N k_B T}{V}$

Entropy :
$$S = - \left(\frac{\partial A}{\partial T} \right)_{N, V} = - \left[\frac{\partial}{\partial T} \left[N k_B T \ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right) - N k_B T \right] \right]_{N, V}$$

$$= N k_B \ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right) + \frac{3}{2} N k_B + N k_B = N k_B \ln \left(\frac{N}{V} \right) \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} + \frac{5}{2} N k_B$$

Internal Energy :
$$U = - \left[\frac{\partial}{\partial \beta} \ln (Q_N(V, T)) \right]_{N, V} = - T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_{N, V} = \frac{3}{2} N k_B T$$

Gibb's free Energy : $G = A + PV = N\mu$

By considering N particles system as independent harmonic oscillator we can solve two important problems.

- (i) The theory of Black body radiation (statistical mechanics of photons)
- (ii) The theory of lattice vibration (statistical mechanics of phonons)

Case-I: When the oscillators can be treated classically

The hamiltonian is given by

$$H(q_i, p_i) = \frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2, \quad i = 1, 2, 3, \dots, N$$

For the single oscillator the partition function will be

$$Q_1(V, T) = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left\{ -\beta \left(\frac{1}{2} m \omega^2 q^2 + \frac{p^2}{2m} \right) \right\} dp dq$$

$$= \frac{1}{h} \left[\int_{-\infty}^{\infty} \exp \left(-\beta \left(\frac{1}{2} m \omega^2 q^2 \right) \right) dq + \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp \right]$$



$$= \frac{1}{h} \left(\frac{2\pi}{\beta m \omega^2} \right)^{1/2} \left(\frac{2\pi m}{\beta} \right)^{1/2} = \frac{1}{\beta \hbar \omega} = (\beta \hbar \omega)^{-1} \left\{ \int_0^\infty e^{-\alpha x^2} x^n dx = \frac{1}{2} \alpha^{-\frac{(n+1)}{2}} \Gamma\left(\frac{n+1}{2}\right) \right\}$$

$$\text{where } \hbar = \frac{h}{2\pi}$$

The partition function of the N-oscillator system is given by

$$Q_N(V, T) = [Q_1(V, T)]^N = (\beta \hbar \omega)^{-N}$$

In this case we have assumed the oscillators to be distinguishable (oscillators can be treated as distinguishable if these oscillator representation of energy levels available in the system or they are not particle (even quasiparticle)).

Oscillators can be treated as indistinguishable if we consider these as particle (Photons or Phonons)

Helmholtz free Energy (A) :

$$A = -k_B T \ln Q_N(V, T)$$

$$= -k_B T \ln (\beta \hbar \omega)^{-N} = N k_B T \ln \beta \hbar \omega = N k_B T \ln \frac{\hbar \omega}{k_B T}$$

Chemical Potential (μ) :

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T, V} = \left(\frac{\partial}{\partial N} N k_B T \ln \frac{\hbar \omega}{k_B T} \right)_{T, V} = k_B T \ln \frac{\hbar \omega}{k_B T}$$

$$\text{Pressure: } P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = 0 \text{ because } A \text{ is independent of } V$$

$$\text{Entropy (s): } S = - \left(\frac{\partial A}{\partial T} \right)_{N, V} = - \left(\frac{\partial}{\partial T} N k_B T \ln \frac{\hbar \omega}{k_B T} \right)_{N, V}$$

$$= N k_B \ln \frac{k_B T}{\hbar \omega} - N k_B = N k_B \left[\ln \frac{k_B T}{\hbar \omega} - 1 \right]$$

$$\text{Internal Energy: } U = - \left(\frac{\partial}{\partial \beta} \ln Q_N(V, T) \right)_{N, V} = - \frac{\partial}{\partial \beta} \ln (\beta \hbar \omega)^{-N} = N \frac{\partial}{\partial \beta} \ln \beta \hbar \omega$$

$$= \frac{1}{\beta \hbar \omega} \times \hbar \omega = \frac{1}{\beta} = N k_B T$$

$$\text{So, } C_V = N k_B$$

$$\text{Gibb's free Energy } G = A + PV = A = N k_B T \ln \left(\frac{\hbar \omega}{k_B T} \right) \quad [\because P = 0]$$

The mean energy per oscillator is in complete agreement with the equipartition theorem i.e. $2 \times \frac{1}{2} k_B T$. For we have here two independent quadratic terms in the single oscillator Hamiltonian.



The density of states $g(E)$ of this system from the expression of partition function we have

$$g(E) = \frac{1}{(\hbar\omega)^N} \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{e^{\beta E}}{\beta^N} d\beta \quad (\beta > 0)$$

$$g(E) = \begin{cases} \frac{1}{(\hbar\omega)^N} \frac{E^{N-1}}{(N-1)!} & \text{for } E \geq 0 \text{ and } 0 \text{ for } E \leq 0 \end{cases}$$

The entropy of the system can be calculate from equation by considering $N \gg 1$ and using Stirling's approximation.

$$S(N, E) = k_B \ln g(E) = k_B \ln \frac{1}{(\hbar\omega)^N} \frac{E^{N-1}}{(N-1)!}$$

$$\text{For } N \gg 1 \quad S = k_B \ln \frac{1}{(\hbar\omega)^N} \frac{E^N}{N!} = k_B \ln \left(\frac{E}{\hbar\omega} \right)^N \frac{1}{N!}$$

$$= k_B \left[N \ln \frac{E}{\hbar\omega} - \ln N! \right] = k_B \left[N \ln \frac{E}{\hbar\omega} - N \log N + N \right]$$

$$= Nk_B \left[\ln \frac{E}{N\hbar\omega} + 1 \right] - (V) \quad T = \left(\frac{\partial S}{\partial E} \right)^{-1} = \frac{E}{N} \quad \text{or} \quad E = Nk_B T$$

Put this value of E in V So we get

$$S = Nk_B \left[\ln \frac{k_B T}{\hbar\omega} + 1 \right] \text{ which is the entropy we are obtaining by using partition function}$$

Case-II: When the oscillators can be treated quantum mechanically

Quantum-mechanically the energy eigenvalues of a one dimensional harmonic oscillator are given by

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \quad n = 0, 1, 2, \dots$$

For single oscillator, the partition function is

$$\begin{aligned} Q_1(\beta) &= \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_n e^{-\beta \left(n + \frac{1}{2} \right) \hbar\omega} \\ &= e^{-\frac{\beta\hbar\omega}{2}} + e^{-\frac{3\beta\hbar\omega}{2}} + e^{-\frac{5\beta\hbar\omega}{2}} + \dots \\ &= e^{-\frac{\beta\hbar\omega}{2}} \left(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots \right) \\ &= \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \left(\frac{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}}{2} \right)} = \left(2 \sinh \left(\frac{\beta\hbar\omega}{2} \right) \right)^{-1} \end{aligned}$$

$$\text{So, } Q_N(V, T) = [Q_1(V, T)]^N = \left[2 \sinh \left(\frac{\beta\hbar\omega}{2} \right) \right]^{-N}$$



Helmholtz free energy :

$$\begin{aligned}
 A &= -k_B T \ln Q_N(V, T) \\
 &= -k_B T \ln \left[2 \sinh \left(\frac{\beta \hbar \omega}{2} \right) \right]^N = N k_B T \ln \left[2 \sinh \frac{\beta \hbar \omega}{2} \right] \\
 A &= N k_B T \ln \left[2 \sinh \frac{\hbar \omega}{2 k_B T} \right], \quad \text{where } \beta = \frac{1}{k_B T}
 \end{aligned}$$

Chemical potential (μ):

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V, T} = k_B T \ln \left(2 \sinh \frac{\hbar \omega}{k_B T} \right)_{V, T} = \frac{A}{N}$$

Pressure: $P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = 0$

Entropy: (S)

$$\begin{aligned}
 S &= - \left(\frac{\partial A}{\partial T} \right)_{N, V} = - \left[N k_B \ln 2 \sinh \frac{\hbar \omega}{k_B T} + N k_B T \frac{1}{\sinh \left(\frac{\hbar \omega}{2 k_B T} \right)} \times \cos \left(\frac{\hbar \omega}{2 k_B T} \right) \times \frac{\hbar \omega}{2 k_B} \times \left(\frac{-1}{T^2} \right) \right] \\
 &= N k_B \left[\frac{1}{2} \beta \hbar \omega \coth \frac{\beta \hbar \omega}{2} - \ln \left\{ 2 \sinh \left(\frac{\beta \hbar \omega}{2} \right) \right\} \right] = N k_B \frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} - \ln (1 - e^{-\beta \hbar \omega})
 \end{aligned}$$

Internal Energy :

$$\begin{aligned}
 U &= -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)_{N, V} = -T^2 \left(\frac{\partial}{\partial T} \left(N k_B \ln 2 \sinh \frac{\hbar \omega}{2 k_B T} \right) \right)_{N, V} \\
 &= \frac{1}{2} N \hbar \omega \coth \left(\frac{\beta \hbar \omega}{2} \right) = N \left[\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]
 \end{aligned}$$

Specific Heat: $C_V = \left(\frac{\partial U}{\partial T} \right)_{N, V} = N k_B \left(\frac{1}{2} \beta \hbar \omega \right)^2 \operatorname{cosec}^2 h \left(\frac{1}{2} \beta \hbar \omega \right)$

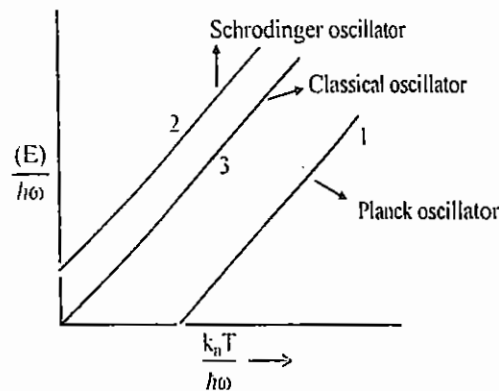
$$= N k_B (\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

Now, $U = N \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right)$

So, $\frac{U}{N} = \left(\frac{1}{2} \hbar \omega + k_B T \right) \quad \text{if } \beta \hbar \omega \ll 1$



Quantum mechanical oscillators does not obey equipartition theorem i.e. mean thermal energy per particle is always greater than $k_B T$. If $k_B T \ll \hbar\omega$ the oscillator is known as Schrodinger oscillator and if $k_B T \gg \hbar\omega$ is known as Planck's oscillator



In case of classical oscillator mean energy = $k_B T$ but in case of Planck's oscillator mean energy $k_B T - \frac{1}{2}\hbar\omega$

Q. Show that the partition function $Q_N(V, T)$ of an extreme relativistic gas consisting of N monoatomic molecules with energy momentum relationship $E = pc$ where $c = \text{speed of light}$, is given by

$$Q_N(V, T) = \frac{1}{N!} \left[8\pi V \left(\frac{k_B T}{hc} \right)^3 \right]^N$$

Study the thermodynamics of the system checking in particular that $PV = \frac{1}{3}U$, $\frac{U}{N} = 3k_B T$, $\gamma = \frac{4}{3}$.

Soln. $Q_N(V, T) = \frac{1}{N!} [Q_1(V, T)]^N = \frac{1}{N!} \left[\frac{1}{h^3} \int e^{-\beta H} d\omega \right]^N$

$$= \frac{1}{N! h^{3N}} \int e^{-\beta pc} d^{3N}p d^{3N}q$$

For extreme relativistic case $H = pc$ and $d\omega = d^{3N}p d^{3N}q$

$$Q_N(V, T) = \frac{V^N}{N! h^{3N}} \left[\int e^{-\frac{pc}{k_B T}} d^{3N}p \right] \left(\int d^{3N}q = \int d^3q_1 d^3q_2 \dots d^3q_N \right)$$

$$= \frac{V^N}{N! h^{3N}} \left[\int_0^\infty e^{-\frac{pc}{k_B T}} 4\pi p^2 dp \right]^N$$

$$= \frac{(4\pi V)^N}{N! h^{3N}} \left[\int_0^\infty e^{-\frac{pc}{k_B T}} p^2 dp \right]^N$$

Let $\frac{pc}{k_B T} = x \Rightarrow \frac{c}{k_B T} dp = dx$

$$Q_N(V, T) = \frac{(4\pi V)^N}{N! h^{3N}} \left[\int_0^\infty e^{-x} \left(\frac{k_B T x}{c} \right)^2 \frac{k_B T}{c} dx \right]^N = \frac{(4\pi V)^N}{N! h^{3N}} \left[\left(\frac{k_B T}{c} \right)^3 \int_0^\infty e^{-x} x^2 dx \right]^N$$



$$= \frac{(4\pi V)^N}{N! h^{3N}} \left[\left(\frac{k_B T}{c} \right)^3 2! \right]^N$$

$$\text{So, } Q_N(V, T) = \frac{1}{N!} \left[8\pi V \left(\frac{k_B T}{hc} \right)^3 \right]^N$$

$$\begin{aligned} \Rightarrow \ln Q_N(V, T) &= N \ln \left(8\pi V \left(\frac{k_B T}{hc} \right)^3 \right) - \log N! = N \ln \left(8\pi V \left(\frac{k_B T}{hc} \right)^3 \right) - N \ln N + N \\ &= N \ln \frac{8\pi V}{N} \left(\frac{k_B T}{hc} \right)^3 + N \end{aligned}$$

$$\text{Now, } A = -k_B T \ln Q_N(V, T) = -Nk_B T \ln \left(\frac{8\pi V}{N} \left(\frac{k_B T}{hc} \right)^3 \right) - Nk_B T$$

$$\text{Now, } P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = Nk_B T \frac{\frac{8\pi}{N} \left(\frac{k_B T}{hc} \right)^3}{\frac{8\pi V}{N} \left(\frac{k_B T}{hc} \right)^3} = \frac{Nk_B T}{V}$$

$$\text{Now, } U = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)_{N, V} = T^2 Nk_B \times \frac{\frac{8\pi V}{N} \left(\frac{k_B}{hc} \right)^3 3T^2}{\frac{8\pi V}{N} \left(\frac{k_B T}{hc} \right)^3} = \frac{3k_B N T^4}{T^3} = 3Nk_B T$$

$$\text{Now, } \frac{P}{U} = \frac{\frac{Nk_B T}{V}}{3Nk_B T} \Rightarrow PV = \frac{U}{3}$$

$$\text{Now, } dQ = dU + PdV$$

$$\text{For adiabatic process, } dQ = 0$$

$$\text{So, } dU + PdV = 0 \Rightarrow d(3PV) + PdV = 0$$

$$\Rightarrow 3PdV + 3VdP + PdV = 0 \quad \text{or} \quad 4PdV = -3VdP$$

$$\Rightarrow \frac{dP}{P} = -\frac{4}{3} \frac{dV}{V}$$

Integrating, we have

$$PV^{4/3} = \text{constant}$$

$$\text{So, we have } \gamma = \frac{4}{3}$$



Q. Consider a system of an extreme relativistic gas consisting of $3N$ particles moving in 1 dimension.

Show that the partition function in this case is given by $\frac{1}{3N!} \left[2L \left(\frac{k_B T}{hc} \right) \right]^{3N}$, L being the length of the space available.

Soln. $Q_N(V, T) = \frac{1}{3N!} [Q_1(V, T)]^{3N} = \frac{1}{3N!} \left[\frac{1}{h} \int_{-\infty}^{\infty} e^{-\beta pc} dp dq \right]^{3N} = \frac{1}{3N! h^{3N}} L^{3N} \left[\int_{-\infty}^{\infty} e^{-\frac{pc}{k_B T}} dp \right]^{3N}$

Let $\frac{pc}{k_B T} = x \Rightarrow dp = \frac{k_B T}{c} dx$

$$Q_N(V, T) = \frac{1}{3N! h^{3N}} L^{3N} \left[2 \int_0^{\infty} e^{-x} \frac{k_B T}{c} dx \right]^{3N}$$

$$= \frac{1}{3N! h^{3N}} L^{3N} \left(\frac{k_B T}{c} \right)^{3N} \left[2 \int_0^{\infty} e^{-x} dx \right]^{3N} = \frac{1}{3N! h^{3N}} L^{3N} \left(\frac{k_B T}{c} \right)^{3N} 2^{3N}$$

So, $Q_N(V, T) = \frac{1}{3N!} \left[2L \left(\frac{k_B T}{hc} \right) \right]^{3N}$

Thermodynamics of Magnetic System

We consider a system of N dipoles with $J = \frac{1}{2}$. There is no interaction among the dipole. The dipole can be oriented in two directions and the corresponding energies are $E = -\mu_B H$ and $E = \mu_B H$ when placed in magnetic field H .

$$Q_N(V, T) = (e^{\beta \epsilon} + e^{-\beta \epsilon})^N = [2 \cosh(\beta \epsilon)]^N = \left[2 \cosh \left(\frac{\mu_B H}{k_B T} \right) \right]^N$$

Helmholtz free energy :

$$A = -k_B T \ln Q_N(V, T) = -k_B T \ln \left(2 \cosh \left(\frac{\mu_B H}{k_B T} \right) \right)^N$$

Pressure(P) :

$$P = \left(\frac{\partial A}{\partial V} \right)_{N, T} = 0$$

Entropy (S) :

$$S = - \left(\frac{\partial A}{\partial T} \right)_{N, V}$$

$$S = Nk_B \left[\ln \left\{ 2 \cosh \left(\frac{\mu_B H}{k_B T} \right) \right\} - \frac{N \mu_B H}{k_B T} \tanh \left(\frac{\mu_B H}{k_B T} \right) \right]$$



Internal energy (U):

$$U = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)_{N,V} = -N\mu_B H \tanh \frac{\mu_B H}{k_B T}$$

Magnetisation (M):

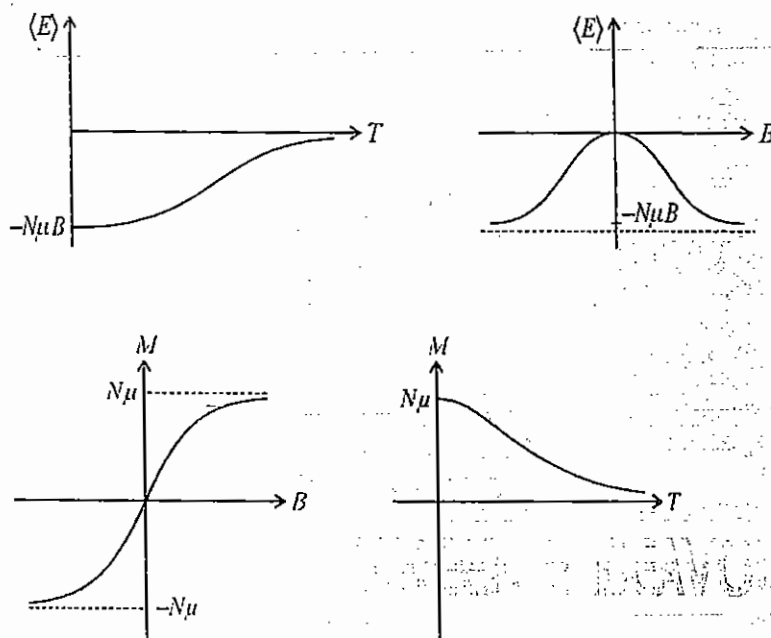
$$M = - \left(\frac{\partial A}{\partial H} \right)_{N,T} = N\mu_B \tanh \frac{\mu_B H}{k_B T}$$

So $U = -M H$

Specific heat (C):

$$C = \left(\frac{\partial U}{\partial T} \right)_{H,N} = Nk_B \left(\frac{\mu_B H}{k_B T} \right)^2 \sec^2 h \left(\frac{\mu_B H}{k_B T} \right)$$

The corresponding graphs are:



Energy fluctuations in the canonical ensemble:

$$(\Delta E)^2 = (E - \langle E \rangle)^2$$

$$\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle + \langle E \rangle^2 - 2\langle E \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$\text{The average energy } \langle E \rangle = U = \langle E_r \rangle = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r) = \sum_r E_r P_r}$$

$$\text{Now } \frac{\partial U}{\partial \beta} = \frac{\partial}{\partial \beta} \langle E_r \rangle = \frac{\partial}{\partial \beta} \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$$



$$\begin{aligned}
 &= - \frac{\sum_r e^{-\beta E_r} \sum_r E_r^2 e^{-\beta E_r} + \left(\sum_r E_r e^{-\beta E_r} \right)^2}{\left(\sum_r e^{-\beta E_r} \right)^2} = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \frac{\left(\sum_r E_r e^{-\beta E_r} \right)^2}{\left(\sum_r e^{-\beta E_r} \right)^2} \\
 &= - \langle E_r^2 \rangle + \langle E_r \rangle^2 = - \langle (\Delta E)^2 \rangle
 \end{aligned}$$

Now $\langle (\Delta E)^2 \rangle = \frac{-\partial U}{\partial \beta} = \frac{\partial U}{\partial T} \times \frac{\partial T}{\partial \beta} = k_B T^2 C_V \Rightarrow \sqrt{\langle (\Delta E)^2 \rangle} = \sqrt{k_B T^2 C_V}$

Relative root mean square fluctuation in E

$$\frac{\sqrt{k_B T^2 C_V}}{E} = \frac{\text{Of the order of } N^{1/2}}{\text{Of the order of } N} = \text{of the order of } N^{-1/2}$$

where N being the number of particles in the system. Consequently for large N (which is true for every statistical system), the relative root mean square fluctuation in the value of energy is quite negligible. Thus for all practical purpose a system in the canonical ensemble has an energy equal to or almost equal to the mean energy U . The situation in this ensemble is therefore practically the same as in the microcanonical ensembles. That explains why the two ensemble lead to the practically identical results.

Grand Canonical Ensemble

Grand canonical ensemble: It is an ensemble in which system can exchange both energy as well as particles with each other or particle energy reservoir.

Equilibrium: We consider the given system A as immersed in a large reservoir A with which it can exchange both energy as well as particles. After some time, both attain the state of mutual equilibrium. In equilibrium both have the same value of T and μ , the number of particle and energy become variable whose values can lie at any particular time t anywhere between 0 to ∞ . If at a particular instant of time, the system A happens to be in one of its states characterized by the number N_r of particles and the amount E_s of energy then the number of particles in the reservoir would be N_r' and its energy E_s' such that

$$\begin{aligned}
 N_r + N_r' &= N^{(0)} = \text{constant} \\
 E_s + E_s' &= E^{(0)} = \text{constant}
 \end{aligned}$$

where, N_r' and E_s' be the number of particles and energy of the reservoir respectively.

Since the reservoir is supposed to be much larger than the given system, we have

$$\frac{N_r}{N^{(0)}} = \left(1 - \frac{N_r'}{N^{(0)}} \right) \ll 1 \quad \text{and} \quad \frac{E_s}{E^{(0)}} = \left(1 - \frac{E_s'}{E^{(0)}} \right) \ll 1$$

The probability P_{rs} that at time t the system A is found to be in an (N_r, E_s) state would be directly proportional to the no. of microstate $\Omega'(N_r', E_s')$ which the reservoir can have for the corresponding macrostate

$$(N_r', E_s')$$

$$\text{So, } P_{rs} \propto \Omega'(N_r', E_s')$$



or, $P_{rs} = C \Omega'(N^{(0)} - N_r, E^{(0)} - E_s)$, where C is proportionality constant

For simplicity of calculation we take the log

$$\ln P_{rs} = \ln \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) + \ln C$$

$$\begin{aligned} \text{Now, } \ln \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) &= \ln \Omega'(N^{(0)}, E^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial N_r} \right)_{N'=N^{(0)}} (-N_r) \\ &\quad + \left(\frac{\partial \ln \Omega'}{\partial E_s} \right)_{E'_s=E^0} (-E_s) + \dots \\ &\approx \ln \Omega'(N^{(0)}, E^{(0)}) + \frac{\mu'}{k_B T} (-N_r) - \frac{1}{k_B T} E_s \end{aligned}$$

$$\text{So, } P_{rs} = A e^{-\alpha N_r - \beta E_s} \text{ where, } \alpha = \frac{-\mu'}{k_B T}, \beta = \frac{1}{k_B T} \text{ and } A \text{ is some constant}$$

$$\text{Using, } 1 = \sum_{rs} P_{rs} = A \sum_{rs} e^{-\alpha N_r - \beta E_s}, \text{ we have } A = \frac{1}{\sum_{rs} e^{-\alpha N_r - \beta E_s}}$$

$$\text{So, we have, } P_r = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{rs} e^{-\alpha N_r - \beta E_s}}$$

Partition function (Z):

$$\begin{aligned} Z(\mu, V, T) &= \sum_{rs} e^{-\alpha N_r - \beta E_s} \\ &= \sum_r \sum_s e^{-\alpha N_r} e^{-\beta E_s} = \sum_{N_r=0}^{\infty} e^{-\alpha N_r} Q_{N_r}(V, T) \\ &= \sum_{N_r=0}^{\infty} (Z)^{N_r} Q_N(V, T) \end{aligned}$$

where, $Z = e^{-\alpha}$ = fugacity of the system

Q. Consider a system may be either unoccupied or occupied by one particle with energy 0 and E . Find out 1) partition function of the system 2) Thermal average energy of the system. Thermal average occupancy of the system

Soln.	0	E	N_r	E_s
	0	0	0	0
	1	0	1	0
	0	1	1	E

$$Z(\mu, V, T) = \sum_{rs} e^{-\alpha N_r - \beta E_s}$$



$$= e^{-\alpha \times 0 - \beta \times 0} + e^{-\alpha \times 1 - \beta \times 0} + e^{-\alpha \times 1 - \beta \times 1}$$

$$1 + e^{-\alpha} + e^{-\alpha - \beta \epsilon} = 1 + e^{\frac{\mu}{k_B T}} + e^{\left(\frac{\mu}{k_B T} - \frac{E}{k_B T}\right)}$$

$$U = \langle E_S \rangle = \frac{\sum_{rs} E_S e^{-\alpha N_r - \beta E_S}}{\sum_{rs} e^{-\alpha N_r - \beta E_S}} = \sum_{rs} E_S P_{rs}$$

$$\text{And, } \bar{N} = \langle N_r \rangle = \frac{\sum_{rs} N_r e^{-\alpha N_r - \beta E_S}}{\sum_{rs} e^{-\alpha N_r - \beta E_S}} = \sum_{rs} N_r P_{rs}$$

Q. Repeat the above problem if each state may be occupied by one particle of the same time

Soln.

0	E	N_r	E_s
0	0	0	0
1	0	1	0
0	1	1	E
0	1	2	E

$$\text{So, } Z_N(\mu, V, T) = 1 + e^{-\alpha} + e^{-\alpha - \beta \epsilon} + e^{-2\alpha - \beta \epsilon}$$

Physical Significance of various statistical quantities

In order to establish a connection between the statistics of the grand canonical ensemble and the thermodynamics of the system we introduce a quantity q defined by

$$q \equiv \ell n Z(\mu, V, T) = q(\alpha, \beta, \epsilon_s)$$

$$dq = \left(\frac{\partial q}{\partial \alpha} \right)_{\beta, E_s} d\alpha + \left(\frac{\partial q}{\partial \beta} \right)_{\alpha, E_s} d\beta + \left(\frac{\partial q}{\partial E_s} \right)_{\alpha, \beta} dE_s$$

$$Z(\mu, V, T) = \sum_{r,s} e^{-\alpha N_r - \beta E_S}$$

$$\ell n Z(\mu, V, T) = -\alpha N_r - \beta E_S$$

$$dq = -\bar{N} d\alpha - \bar{E} d\beta - \frac{\beta}{N} \sum < n_{rs} > dE_s$$

Now we consider an ensemble of N identical system (labelled 1, 2...N mutually sharing a total number of particle $N\bar{N}$ and total energy $N\bar{E}$. Let n_{rs} be the no. of system that have at any time t the number of particle N_r and amount of energy E_s

$$\sum_{r,s} n_{rs} = N$$

$$\sum_{r,s} n_{rs} N_r = N\bar{N}$$



And
$$\sum_{r,s} \eta_{rs} E_s = N \bar{E}$$

$$q = \ell n Z(Z, V, T) = \ell n \left[\sum_{r,s} e^{-\alpha N_r - \beta E_s} \right]$$

$$\frac{\partial q}{\partial E_s} = \frac{\sum_{r,s} -\beta e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = \beta \sum_{r,s} \frac{\langle \eta_{r,s} \rangle}{N}$$

So
$$Pr,s = \frac{\langle \eta_{r,s} \rangle}{N} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

Add on both side $\alpha d\bar{N} + \beta d\bar{E}$

$$\begin{aligned} d(q + \bar{N}\alpha + \beta\bar{E}) &= \alpha d\bar{N} + \beta d\bar{E} - \beta/N \sum_{r,s} \langle \eta_{r,s} \rangle dE_s \\ &= \beta \left(\frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \frac{1}{N} \sum_{r,s} \langle \eta_{r,s} \rangle dE_s \right) \end{aligned}$$

To interpret each term in right hand side bracket we compare this by

$$dQ = d\bar{E} + Pd\bar{V} - \mu d\bar{N}$$

So
$$\frac{\alpha}{\beta} = -\mu \quad dW = -\frac{1}{N} \sum_{r,s} \langle \eta_{r,s} \rangle dE_s \quad d\bar{E} = d\bar{E}$$

So
$$\begin{aligned} d(q + \bar{N}\alpha + \beta\bar{E}) &= \beta(-\mu d\bar{N} + d\bar{E} + dW) = \\ &= \beta(dQ) = \beta T dS \end{aligned}$$

On integrating both side

$$\begin{aligned} q + \alpha\bar{N} + \beta\bar{E} &= \beta TS \\ q &= \frac{S}{k_B} - \alpha\bar{N} - \beta\bar{E} \quad \left(\beta TS = \frac{1}{k_B T} \cdot TS = \frac{S}{k_B} \right) \\ &= \frac{S}{k_B} + \frac{\mu}{k_B T} \bar{N} - \frac{\bar{E}}{k_B T} \\ &= \frac{TS + \mu\bar{N} - \bar{E}}{k_B T} = \frac{TS + G - U}{k_B T} \quad (\because \bar{E} = U \quad \mu\bar{N} = G) \end{aligned}$$

Now $G = A + PV$

So
$$q = \frac{TS + A + PV - U}{k_B T} = \frac{PV}{k_B T} \quad (\because U = A + TS)$$

$$q = \frac{PV}{k_B T}$$



$$p = \frac{k_B T}{V} q = \frac{k_B T}{V} \ln Z(z, V, T)$$

$$\bar{N} = -\frac{\partial}{\partial \alpha} \ln Z(z, V, T) = -\left(\frac{\partial q}{\partial \alpha}\right)_{V, T}$$

$$U = \bar{E} = -\left(\frac{\partial q}{\partial \beta}\right)_{z, V} = k_B T^2 \left[\frac{\partial}{\partial T} q(z, V, T) \right]_{z, V}$$

$$Z = e^{-\alpha} = e^{\mu/k_B T}$$

$$\ln z = \frac{\mu}{k_B T} \Rightarrow \mu = k_B T \ln z, A = \mu N - PV = N k_B T \ln z - k_B T q$$

$$G = \mu N = N k_B T \ln z, S = -\left(\frac{\partial A}{\partial T}\right) = -N k_B \ln z + k_B q$$

Classical ideal gas : We consider a classical ideal gas consisting of N non-interacting particles

$$Z(z, V, T) = \sum_{n_r=0}^{\infty} Z^{n_r} Q_{n_r}(V, T)$$

$$Q_{n_r}(V, T) = [Q_1(V, T)]^{n_r} = \frac{1}{n_r!} \left(\frac{V}{\lambda^3}\right)^{n_r} = \frac{[V f(T)]^{n_r}}{n_r!}$$

$\left[Q_1(V, T) = \frac{1}{n_r!} \left(\frac{V}{\lambda^3}\right) \right]$ as λ is function of temperature which is diff for difference case (relativistic, non-relativistic). So We write $\lambda^3 = f(T)$

$$Z(z, V, T) = \sum_{n_r=0}^{\infty} \frac{\{z V f(T)\}^{n_r}}{n_r!}$$

Let $z V f(T) = x$

For diff value N i.e. 0, 1, 2,?

$$= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

$$= \exp[z V f(T)] = e^x = e^{[V f(T)]}$$

$$q = \ln Z(z, V, T) = \ln \exp[z V f(T)] \Rightarrow \boxed{q = z V f(T)}$$

$$p = \frac{k_B T}{V} q(z, V, T) = \frac{k_B T}{V} z V f(T) = z k_B T f(T)$$

$$N = z \left(\frac{\partial q}{\partial Z} \right)_{V, T} = z V f(T)$$

$$U = k_B T^2 \left(\frac{\partial q}{\partial T} \right) = k_B T^2 z V f'(T)$$

$$A = N k_B T \ln Z - z k_B T V f(T)$$

$$S = -\left(\frac{\partial A}{\partial T}\right) = -N k_B \ln Z + z k_B V f(T) + z k_B V f(T)$$



Eliminating z from the expression of P and N we get

$$PV = Nk_B T \quad (\text{Classical ideal gas})$$

Eliminating Z from N and U we get $U = Nk_B T^2 \frac{f'(T)}{f(T)}$

If $f(T) \propto T^n$ then

$$U = Nk_B T^2 \times \frac{nT^{n-1}}{T^n} = nNk_B T$$

$$C_V = \frac{\partial U}{\partial T} = nNk_B$$

$$P \propto \frac{U}{V} \Rightarrow P = \frac{1}{n} \frac{U}{V}$$

$$n = \frac{3}{2} \text{ for non-relativistic classical ideal gas}$$

$$n = 3 \text{ for relativistic classical ideal gas.}$$

Harmonic oscillator :

$$Q_1(V, T) = V f(T) \text{ for indistinguishable particle}$$

$$= f(T) \text{ for distinguishable particle}$$

Particle density and energy fluctuation in grand canonical ensemble (Correspondance with other ensmeble)

In the grandcanonical ensemble the variable N & E for any member of the ensemble can lie between 0 to ∞ . So grandcanonical ensemble appears to be very different from other ensemble (microcanonical and canonical). However the thermodynamical results are same for these three ensemble. Thus inspite of the strong facial difference, the overall behaviour of a given physical system is practically the same whether it belongs to one kind of ensemble or another. The basic reason for this is that the relative fluctuation in the values of the quantities that vary from member to member in an ensemble are practically negligible. Therefore inspite of the different surrounding which different ensemble provide to a given physical system, the overall behaviour of the system is not significantly affected.

$$\text{Average number of particle, } \bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

$$\text{Now } \left(\frac{\partial \bar{N}}{\partial \alpha} \right)_{\beta E_s} = \frac{-\sum_{r,s} e^{-\alpha N_r - \beta E_s} \sum_{r,s} N_r^2 e^{-\alpha N_r - \beta E_s} + \left(\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s} \right)^2}{\left(\sum_{r,s} e^{-\alpha N_r - \beta E_s} \right)^2}$$

$$= -\frac{\sum_{r,s} N_r^2 e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} + \frac{\left(\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s} \right)^2}{\left(\sum_{r,s} e^{-\alpha N_r - \beta E_s} \right)^2}$$



$$= -\langle N_r^2 \rangle + \langle N_r \rangle^2 \quad \dots (1)$$

But $(\Delta N)^2 = (N - \langle N \rangle)^2$

$$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle + \langle N \rangle^2 - 2\langle N \rangle^2 = \langle N^2 \rangle - \langle N \rangle^2 \quad \dots (2)$$

Comparing (1) and (2)

$$\left(\frac{\partial \bar{N}}{\partial \alpha} \right)_{\beta, E_S} = -\langle (\Delta N)^2 \rangle$$

$$\langle (\Delta N)^2 \rangle = -\left(\frac{\partial \bar{N}}{\partial \alpha} \right)_{\beta, E_S} = -\left(\frac{\partial \bar{N}}{\partial \alpha} \right)_{T, E_S} = k_B T \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V}$$

As we know $n = \frac{N}{V}$

So $\frac{\langle (\Delta n)^2 \rangle}{n^2} = \frac{\langle (\Delta N)^2 \rangle}{\bar{N}^2} = \frac{k_B T}{\bar{N}^2} \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V}$

$$= \frac{k_B T}{V^2 \left(\frac{\bar{N}^2}{V^2} \right)} V \left(\frac{\partial \frac{\bar{N}}{V}}{\partial \mu} \right)_{T, V} = \frac{k_B T}{V^2} v^2 V \left(\frac{\partial \left(\frac{1}{v} \right)}{\partial \mu} \right)_{T, V} \quad \left(\because v = \frac{V}{\bar{N}} \right)$$

$$= \frac{k_B T}{V^2} v^2 V \left(\frac{\partial \left(\frac{1}{v} \right)}{\partial v} \frac{\partial v}{\partial \mu} \right)_{T, V} = \frac{k_B T}{V^2} v^2 V \times -\frac{1}{v^2} \left(\frac{\partial v}{\partial \mu} \right)_{T, V} = -\frac{k_B T}{V} \left(\frac{\partial v}{\partial \mu} \right)_{T, V}$$

Now, $G = A + VP \Rightarrow dG = TdS - PdV - SdT - TdS + PdV + VdP = -SdT + VdP$

$$\Rightarrow d\left(\frac{G}{N}\right) = -\frac{S}{N} dT + \frac{V}{N} dP$$

$\Rightarrow d\mu = -s dT + vdP$ where, s is entropy per particle and v is volume per particle

At constant temperature $dT = 0 \Rightarrow d\mu = vdP$

So $\frac{\langle (\Delta n)^2 \rangle}{n^2} = -\frac{k_B T}{V} \left(\frac{\partial v}{\partial \mu} \right)_{T, V} = -\frac{k_B T}{V} \frac{1}{v} \left(\frac{\partial v}{\partial P} \right) \quad (\because d\mu = vdP)$

$$\frac{\langle (\Delta n)^2 \rangle}{n^2} = -\frac{k_B T}{V} \kappa_T \quad \text{where } \kappa_T \text{ is the isothermal compressibility}$$

\approx of the order of $\frac{1}{N}$



The relative root mean square fluctuation in the particle density of the given system is of order $N^{-1/2}$. For large values of number of particle relative root mean square fluctuation in the particle density are negligible. There are exception in the situation like phase transition. In these situation the compressibility of a given system can become excessively large. Under these circumstances the isothermal compressibility can very well be of the order of N , the relative root mean square fluctuation in particle density n can then be order of $O(1)$. Thus in the region of phase transition, especially at the critical points, large fluctuation in particle density exist and account for phenomena like critical opalescence. Under these circumstance the formalism of grand canonical ensemble leads to the result that are not identical which the ones following from the corresponding canonical ensemble. It is clear that in such cases the formalism of grand canonical ensemble have to be preferred because only this one will provide a correct picture of the actual physical situation.

Diatomic Molecule

If there are N atoms in a molecule and are rigidly bound together, then there must be $3N$ degree of freedom. For each molecule out of these, 3 corresponding to translational motion of the molecule and 3 or less than 3 corresponds to rotational motion, and corresponds to vibrational mode for non-linear polyatomic ($3N-6$) for linear polyatomic ($3N-5$).

Thermodynamic Properties of a diatomic molecule :

If change in energy (ΔE) $< k_B T$ between two successive level, then energy level variation can be treated as continuous and classical description is applicable. If $\Delta E > k_B T$ then energy variation can be treated as discontinuous and quantum description is applicable.

If a molecule has translational, rotational & vibrational motion, then the partition function of the molecule can be written as

$$Z = Z_t Z_r Z_v \quad \text{or} \quad Q = Q_t Q_r Q_v$$

Now consider a gas of N diatomic non-interacting molecules. Then,

Translational partition function :

$$Z_t = \frac{V}{h^3} (2\pi m k_B T)^{3/2} = \frac{V}{\lambda^3}$$

For a gas of N diatomic molecule, $Z_t = \left(\frac{Z_{1t}}{N!} \right)^N$

$$\begin{aligned} \text{So,} \quad \ell n Z_t &= \ell n \left[\frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \right] = \ell n \left(\frac{V}{\lambda^3} \right)^N - \ell n N! \\ &= N \ell n \frac{V}{\lambda^3} - N \ell n N + N = N \ell n \left(\frac{V}{N \lambda^3} \right) + N \end{aligned}$$

Helmholtz free energy :

$$\begin{aligned} A &= -k_B T \ell n Z_t = -k_B T \left[N \ell n \left(\frac{V}{N \lambda^3} \right) + N \right] \\ &= N T k_B \left[\ell n \left(\frac{N \lambda^3}{V} \right) - 1 \right] = N k_B T \left[\ell n \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} - 1 \right] \end{aligned}$$



Internal energy :

$$U = - \left(\frac{\partial}{\partial \beta} \ln Z_t \right)_{N,V} \quad \text{or} \quad -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)_{N,V} = \frac{3}{2} Nk_B T$$

Specific heat :

$$C = \left(\frac{\partial U}{\partial T} \right)_{N,V} = \frac{3}{2} Nk_B$$

Rotational partition function :

$$Z = \sum_r g_r e^{-\beta E_r} \quad \text{But} \quad E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\text{So, } Z_{lr} = \sum_J (2J+1) e^{-\beta E_r}$$

Where I = moment of inertia, J = rotational quantum number.

The summation can't be change into intergration for small value of I and T but for large value of I and T . The energy separation between the level is small and we can change summation into integration and we can calculate the approximate value of rotational partition function.

$$Z_{lr} = \int_0^\infty 2J e^{-\frac{h^2 J^2}{8\pi^2 I k_B T}} dJ \Rightarrow Z_{lr} = \frac{8\pi^2 I k_B T}{h^2} \Rightarrow Z_r = (Z_{lr})^N = \left(\frac{8\pi^2 I k_B T}{h^2} \right)^N$$

Helmholtz free energy (A) :

$$A = -k_B T \ln Z_r = -k_B T \ln \left(\frac{8\pi^2 I k_B T}{h^2} \right)^N = -Nk_B T \ln \frac{8\pi^2 I k_B T}{h^2}$$

Internal energy (U) :

$$U = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)_{N,V} = Nk_B T$$

Vibrational partition function :

$$Z_{lv} = \sum g_v e^{-\beta E_v} \quad \text{where, } g_v = 1 \text{ for one dimensional harmonic oscillator}$$

$$= \sum e^{-\beta \left(n + \frac{1}{2} \right) \hbar \omega}$$

$$= \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

$$\text{So, } Z_v = (Z_{lv})^N = \left(\frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} \right)^N$$

$$A = -k_B T \ln Z_v = \ln \left(\frac{e^{\frac{-\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}} \right) \text{ and } U = \langle E \rangle = \frac{1}{2} N \hbar \omega + \frac{N \hbar \omega}{e^{k_B T} - 1}$$



Classical Oscillator

For each degree of freedom mean thermal energy for translational motion is $\frac{1}{2}k_B T$, for rotational motion is $\frac{1}{2}k_B T$ and for vibrational motion $k_B T$.

Nuclear spin effect in diatomic molecule:

Partition function for heteronuclear diatomic molecule is

$$Z_r = (2S_1 + 1)(2S_2 + 1) \frac{8\pi^2 I k_B T}{h^2}$$

Partition function for homonuclear diatomic molecule

$$Z_r = (2S + 1)^2 \times \frac{1}{2} \frac{8\pi^2 I k_B T}{h^2} = (2S + 1)^2 \frac{4\pi^2 I k_B T}{h^2}$$

In a homonuclear diatomic molecule the two atoms will be of same kind. They have same spin. The spin of two same atom may be either parallel or antiparallel. If spins are parallel then resultant spin is one (ortho) and for antiparallel spin, resultant spin is zero (para).

Now in general if the spin of each nuclei is I . The resultant spin of the diatomic molecule will be either $2I$ for parallel arrangement or zero for antiparallel arrangement. The possible values are $2I, 2I - 2, \dots, 2, 1, 0$

So, $S = 2I - n$ $n = 0, 1, 2$

Now, Statistical weight factor for ortho = $\sum_n 2(2I - n) + 1$, $n = 0, 2, 4$

$$= 4I + 1 + 4I - 3 + 4I - 7 \dots \dots \dots 3$$

$$= \frac{(2I + 1)}{4} (4I + 1 + 3) = (2I + 1)(I + 1)$$

Statistical weight factor for para = $\sum_n 2(2I - n) + 1$, $n = 1, 3, 5$

$$= 4I - 1 + 4I - 5 + 4I - 9 \dots \dots \dots 1$$

$$= \frac{(2I + 1)}{4} (4I - 1 + 1) = I(2I + 1)$$

$$Z_r = \text{Statistical weight factor} \times \sum_J (2J + 1) e^{-\frac{J(J+1)h^2}{8\pi^2 I k_B T}}$$

$$= (2I + 1)(I + 1) \sum_{J=1,3,5} (2J + 1) e^{-\frac{J(J+1)h^2}{8\pi^2 I k_B T}} + (2I + 1) \sum_{J=0,2,4} (2J + 1) e^{-\frac{J(J+1)h^2}{8\pi^2 I k_B T}}$$

$$= ((2I + 1)(I + 1) + I(2I + 1)) \frac{8\pi^2 I k_B T}{2h^2} \Rightarrow Z_r = (2I + 1)^2 \frac{4\pi^2 I k_B T}{h^2}$$



Average Thermal Energy for a linear Polyatomic Molecule

(I) for linear polyatomic molecule, the degree of freedom is

$$F = \underbrace{\frac{3}{2}k_B T}_{\text{Translational}} + 2 \times \underbrace{\frac{1}{2}k_B T}_{\text{Rotational}} + \underbrace{(3N-5)k_B T}_{\text{Vibrational}} = (6N-5) \frac{k_B T}{2}$$

(II) for non linear polyatomic molecule, the degree of freedom is

$$F = \frac{3}{2}k_B T + 3 \times \frac{1}{2}k_B T + (3N-6)k_B T = (6N-6) \frac{k_B T}{2}$$

Specific heat:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = (6N-6) \frac{k_B}{2}$$

Q. In a system in thermal equilibrium at absolute temperature T , two states with energy difference $4.83 \times 10^{-23} \text{ J}$ occur with relative probability e^2 . Deduce the temperature ($k_B = 1.38 \times 10^{-23} \text{ J/K}$).

Soln.

$$\Delta E = 4.83 \times 10^{-23}$$

$$\text{So, } \frac{P_1}{P_2} = e^2$$

$$P_1 = C e^{-\beta E_1}$$

$$P_1 = C e^{-\beta E_1}, \quad P_2 = C e^{-\beta E_2}$$

$$\text{So, } \frac{P_1}{P_2} = \frac{C e^{-\beta E_1}}{C e^{-\beta E_2}} = e^{-\beta(E_1 - E_2)} = e^{\beta(E_2 - E_1)}$$

$$\text{So, } e^2 = e^{\beta(E_2 - E_1)}$$

$$\Rightarrow 2 = \beta(E_2 - E_1) \Rightarrow 2 = \frac{1}{k_B T} (E_2 - E_1)$$

$$\Rightarrow 2k_B T = E_2 - E_1 \Rightarrow T = \frac{E_2 - E_1}{2k_B} = \frac{4.83 \times 10^{-23} \text{ J}}{2 \times 1.38 \times 10^{-23} \text{ J/K}} = 1.75 \text{ K}$$

Q. A diatomic gas in thermal equilibrium have temperature 500 K . Its rotational constant 2.0 cm^{-1} . Calculate the relative populations in the rotational states.

Soln. $E = \frac{h^2}{8\pi^2 I} J(J+1)$ where, $B = \frac{h}{8\pi^2 I C}$

$$\text{So, } E = B h c J(J+1)$$

$$\text{Now, } N_J = \frac{N(2J+1)e^{-\beta E_J}}{\sum_J e^{-\beta E_J}}$$

$$\text{But } B h c = 3.96 \times 10^{-16} \text{ erg.}$$

$$\text{So, } \frac{N_{10}}{N_0} = 91.28 \text{ and } \frac{N_{20}}{N_0} = 3.371 \text{ Ans}$$



PREVIOUS YEARS SOLUTIONS OF TIFR

- Q. Hydrogen atoms in the atmosphere of a star are in thermal equilibrium, with an average kinetic energy of 1 eV. The ratio of the number of hydrogen atoms in the 2nd excited state ($n = 3$) to the number in the ground state ($n = 1$) is [TIFR 2017]

(a) 3.16×10^{-11} (b) 1.33×10^{-8} (c) 3.16×10^{-8} (d) 5.62×10^{-6}

Soln. The average thermal kinetic energy of a hydrogen atom is

$$E = \frac{3}{2} k_B T = 1 \text{ eV} \Rightarrow k_B T = \frac{2}{3} \text{ eV}$$

$$\text{Therefore, required ratio} = \frac{N_{n=3}}{N_{n=1}} = \frac{e^{-E_3/k_B T}}{e^{-E_1/k_B T}}, \text{ where } E_n = -\frac{13.6}{n^2} \text{ eV}$$

$$\text{Therefore, required ratio} = \exp \left[\left(\frac{13.6}{9} - \frac{13.6}{1} \right) \frac{1}{\frac{2}{3}} \right] = 1.33 \times 10^{-8}$$

Correct option is (b)

- Q. In a monatomic gas, the first excited state is only 1.5 eV above the ground state, while the other excited states are much higher up. The ground state is doubly-degenerate, while the first excited state has a four-fold degeneracy. If now, the gas is heated to a temperature of 7000 K, the fraction of atoms in the excited state will be approximately [TIFR 2015]

(a) 0.14 (b) 0.07 (c) 0.42 (d) 0.3

Soln. The fraction of atoms in the excited state is

$$\text{Fraction} = \frac{4e^{-(E+1.5)/k_B T}}{2e^{-E/k_B T} + 4e^{-(E+1.5)/k_B T}}$$

$$g = 4 \quad E_2 = E + 1.5 \text{ eV}$$

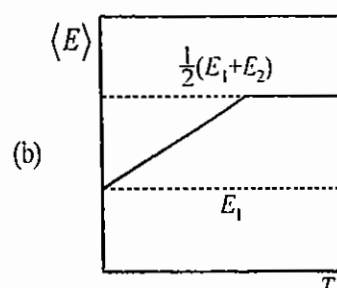
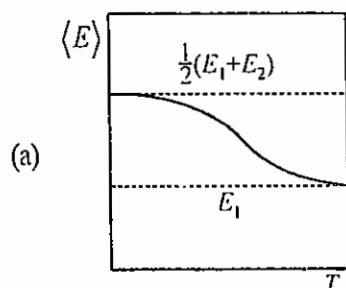
$$g = 2 \quad E_1 = E$$

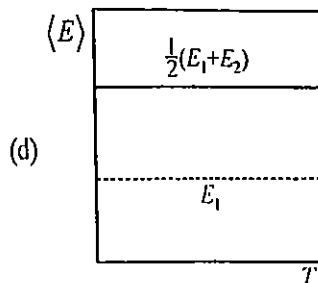
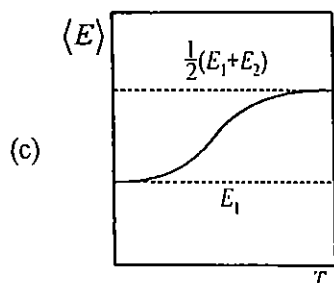
$$\text{where } k_B T = \frac{1.38 \times 10^{-23} \times 7000}{1.6 \times 10^{-19}} \text{ eV} = 0.6 \text{ eV}$$

$$\text{Therefore, fraction} = \frac{2e^{-1.5/0.6}}{1 + 2e^{-1.5/0.6}} = 0.14$$

Correct option is (a)

- Q. Consider an ensemble of microscopic quantum mechanical systems with two energy levels E_1 and E_2 , where $E_1 < E_2$. Which of the following graphs best describes the temperature dependence of the average energy $\langle E \rangle$ of the system? [TIFR 2013]





Soln. The average energy of the system is

$$\langle E \rangle = \frac{E_1 e^{-E_1/k_B T} + E_2 e^{-E_2/k_B T}}{e^{-E_1/k_B T} + e^{-E_2/k_B T}} = \frac{E_1 + E_2 e^{-(E_2 - E_1)/k_B T}}{1 + e^{-(E_2 - E_1)/k_B T}}$$

At low temperature, $\frac{E_2 - E_1}{k_B T}$ is very large, so we have $\exp\left[-\left(\frac{E_2 - E_1}{k_B T}\right)\right] \ll 1$

Therefore, $\langle E \rangle = E_1$

At high temperature, $\frac{E_2 - E_1}{k_B T}$ is very low, so we have $\exp\left[-\left(\frac{E_2 - E_1}{k_B T}\right)\right] \approx 1$.

Therefore, $\langle E \rangle \approx \frac{E_1 + E_2}{2}$.

Correct option is (c)

Q. A classical ideal gas of atoms with masses m is confined in a three-dimensional potential [TIFR 2018]

$$V(x, y, z) = \frac{\lambda}{2} (x^2 + y^2 + z^2)$$

at a temperature T . If k_B is the Boltzmann constant, the root mean square (r.m.s.) distance of the atoms from the origin is

- (a) $\left(\frac{3k_B T}{\lambda}\right)^{1/2}$ (b) $\left(\frac{3k_B T}{2\lambda}\right)^{1/2}$ (c) $\left(\frac{2k_B T}{3\lambda}\right)^{1/2}$ (d) $\left(\frac{k_B T}{\lambda}\right)^{1/2}$

Soln. The given potential is $V(x, y, z) = \frac{\lambda}{2} (x^2 + y^2 + z^2)$

Using law of equipartition of energy, we have

$$\left\langle \frac{\lambda}{2} (x^2 + y^2 + z^2) \right\rangle = \frac{3}{2} k_B T \Rightarrow \frac{\lambda}{2} \langle r^2 \rangle = \frac{3}{2} k_B T$$

$$r_{\text{r.m.s.}} = \sqrt{\langle r^2 \rangle} = \sqrt{\frac{3k_B T}{\lambda}}$$

Correct option is (a)

Q. An system at temperature T has three energy states $0, \pm \epsilon$. The entropy of the system in the low temperature ($T \rightarrow 0$) and high temperature ($T \rightarrow \infty$) limits are, respectively, [TIFR 2013]

- (a) $S_{T \rightarrow 0} = 0$ and $S_{T \rightarrow \infty} = k_B \exp(-3)$ (b) $S_{T \rightarrow 0} = S_{T \rightarrow \infty} = k_B \ln 3$
 (c) $S_{T \rightarrow 0} = 0$ and $S_{T \rightarrow \infty} = k_B \ln 3$ (d) $S_{T \rightarrow 0} = 0$ and $S_{T \rightarrow \infty} = 3k_B / 2$

Soln. The free energy is given by



$$F = -k_B T \ln Z$$

$$= -k_B T \ln (e^{+\beta\epsilon} + 1 + e^{-\beta\epsilon})$$

$$\text{where } \beta = \frac{1}{k_B T}$$

$$\text{The entropy is given by } S = - \left(\frac{\partial F}{\partial T} \right)_V$$

$$\Rightarrow S = \frac{\partial}{\partial T} \left\{ k_B T \ln (e^{\epsilon/k_B T} + 1 + e^{-\epsilon/k_B T}) \right\}$$

$$\Rightarrow S = k_B \ln (e^{\epsilon/k_B T} + 1 + e^{-\epsilon/k_B T}) + k_B T \frac{\left(-\frac{\epsilon}{k_B T^2} e^{\epsilon/k_B T} + \frac{\epsilon}{k_B T^2} e^{-\epsilon/k_B T} \right)}{e^{\epsilon/k_B T} + 1 + e^{-\epsilon/k_B T}}$$

$$= k_B \ln (e^{\epsilon/k_B T} + 1 + e^{-\epsilon/k_B T}) - \frac{\epsilon}{T} \frac{e^{\epsilon/k_B T} - e^{-\epsilon/k_B T}}{e^{\epsilon/k_B T} + 1 + e^{-\epsilon/k_B T}}$$

At low temperature, ($T \rightarrow 0$), $e^{\epsilon/k_B T}$ is large and $e^{-\epsilon/k_B T}$ is low.

$$\text{Therefore, } S = k_B \ln (e^{\epsilon/k_B T}) - \frac{\epsilon}{T} \frac{e^{\epsilon/k_B T}}{e^{\epsilon/k_B T}} = 0$$

At high temperature, ($T \rightarrow \infty$), $e^{\pm \epsilon/k_B T} \approx 1$.

Therefore, $S = k_B \ln 3$.

Correct option is (c)

- Q. When a gas is enclosed in an impermeable box and heated to a high temperature T , some of the neutral atoms lose an electron and become ions. If the number density of neutral atoms, ions and electrons is N_a , N_i and N_e , respectively, these can be related to the average volume V_a occupied by an atom/ion and the ionisation energy E by the relation. [TIFR 2012]

- (a) $N_e(N_a + N_i) = (N_a/V_a) \exp(-E/k_B T)$ (b) $N_a(N_e + N_i) = (N_a/V_a) \exp(-E/k_B T)$
 (c) $N_e N_i = (N_a/V_a) \exp(+E/k_B T)$ (d) $N_e N_i = (N_a/V_a) \exp(-E/k_B T)$

Soln. The number of free electrons per unit volume (N_e) in the gas is equal to the number of bound electrons per unit volume in the atoms times e raised to the power minus of ionisation energy over $k_B T$. Mathematically,

$$N_e = (N_e)_{\text{bound}} e^{-E/k_B T}$$

Now, the total number of places that we could put the electrons is apparently $N_a + N_i$ and since V_a is the volume occupied by an atom/ion, the total amount of volume which is available to bound electrons is

$$(N_a + N_i)V_a. \text{ So the total number of bound electrons per unit volume is } (N_e)_{\text{bound}} = \frac{N_a}{(N_a + N_i)V_a}.$$

$$\text{Therefore, } N_e = \frac{N_a}{(N_a + N_i)V_a} e^{-E/k_B T}.$$



But since the sites in the atoms are already occupied, the another electron does not have all the free sites in it.

$$\text{So, } N_e = \frac{N_a}{N_i V_a} e^{-E/k_B T} \text{ or } N_e N_i = \frac{N_a}{V_a} e^{-E/k_B T}.$$

This is called Saha Ionisation equation.

Correct option is (d)

- Q.** A classical ideal gas, consisting of N particles ($N \rightarrow \infty$) is confined in a box of volume V at temperature T and pressure p . The probability that, at any instant of time, a small sub-volume v_0 becomes totally void (i.e. no particles inside), due to a spontaneous statistical fluctuation, is [TIFR 2013]

(a) $\exp\left(\frac{-v_0}{V}\right)$ (b) $\exp\left(\frac{-Nv_0}{V}\right)$ (c) $\frac{v_0}{V} \exp\left(\frac{-pV}{NT}\right)$ (d) $\frac{pv_0}{NT}$

Soln. Probability of finding one particles in volume v_0 is v_0/V , and to find it elsewhere is $\left(1 - \frac{v_0}{V}\right)$.

Therefore, probability of find no particle in volume v_0 .

$$= \left(1 - \frac{v_0}{V}\right)^N = \exp\left[N \ln\left(1 - \frac{v_0}{V}\right)\right]$$

For small $\frac{v_0}{V}$, $\ln\left(1 - \frac{v_0}{V}\right) \approx -\frac{v_0}{V}$.

Therefore, required probability = $\exp\left[-\frac{N}{V}v_0\right]$.

Correct option is (b)

- Q.** N -particles are distributed among three energy levels having energies: 0 , $k_B T$ and $2k_B T$ respectively. If the total equilibrium energy of the system is approximately $42.5 k_B T$ then find the value of N (to the closest integer). [TIFR 2018]

Soln. The total equilibrium energy is

$$\langle E \rangle = N \frac{\sum_i E_i g_i e^{-E_i/k_B T}}{\sum_i g_i e^{-E_i/k_B T}}$$

$$\Rightarrow 42.5 k_B T = N \left[\frac{k_B T e^{-1} + 2k_B T e^{-2}}{1 + e^{-1} + e^{-2}} \right]$$

$$\Rightarrow N = 42.5 \left[\frac{e^2 + e + 1}{e + 2} \right] = 100.05 \approx 100 \text{ (nearest integer).}$$

Correct answer is (100)

- Q.** Two identical bosons may occupy any of two energy levels 0 , ϵ , where $\epsilon > 0$. The lowest energy state is doubly-degenerate and the excited state is non-degenerate. Assume that the two-particle system is in thermal

equilibrium at a temperature T . Calculate the average energy $\langle E \rangle$. What will be the leading term of $\frac{\langle E \rangle}{\exp\left(-\frac{\epsilon}{k_B T}\right)}$

at low temperature?

[TIFR 2017]



Soln. The average energy is

$$\begin{aligned}\langle E \rangle &= \frac{\sum_i E_i g_i e^{-E_i/k_B T}}{\sum_i g_i e^{-E_i/k_B T}} \\ &= \frac{3.0 e^{-0/k_B T} + 2\epsilon e^{-\epsilon/k_B T} + 2\epsilon e^{-2\epsilon/k_B T}}{3e^{-0/k_B T} + 2e^{-\epsilon/k_B T} + e^{-2\epsilon/k_B T}} \\ &= \frac{2\epsilon (e^{\epsilon/k_B T} + 1)}{3e^{2\epsilon/k_B T} + 2e^{\epsilon/k_B T} + 1}\end{aligned}$$

0	0	ϵ	ϵ_{Total}
..			0
	..		0
		..	2 ϵ
.	.		0
.		.	ϵ
	.	.	ϵ

At low temperature, we have

$$\begin{aligned}\langle E \rangle &\approx 2\epsilon \frac{(e^{\epsilon/k_B T})}{3e^{2\epsilon/k_B T}} \\ \Rightarrow \frac{\langle E \rangle}{e^{-\epsilon/k_B T}} &= \frac{2\epsilon}{3}\end{aligned}$$

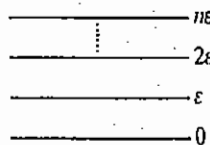
Therefore, the leading term is $2\epsilon/3$.

Correct answer is $(2\epsilon/3)$

- Q.** A statistical system, kept at a temperature T , has n discrete energy levels with equal level spacing ϵ , starting from the energy 0. If, now, a single particle is placed in the system what will be the mean energy of the system in the limit as $n \rightarrow \infty$? [The answer should not be left as a summation]. **[TIFR 2018]**

Soln. The partition function of one particle is

$$\begin{aligned}Z_1 &= \sum_i g_i e^{-\beta E_i} \\ &= 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \dots \\ &= \frac{1}{1 - e^{-\beta\epsilon}} \\ \therefore \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z = \frac{\epsilon e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} \\ &= \frac{\epsilon}{e^{\beta\epsilon} - 1}\end{aligned}$$



Correct answer is $(\epsilon/(e^{\beta\epsilon} - 1))$



PREVIOUS YEARS SOLUTIONS OF JEST

- Q. Consider a system of two particles A and B. Each particle can occupy one of three possible quantum states $|1\rangle, |2\rangle$, and $|3\rangle$. The ratio of the probability that the two particles are in the same state to the probability that the two particles are in different states is calculated for bosons and classical (Maxwell-Boltzmann) particles. They are respectively [JEST 2013]
- (a) 1,0 (b) 1/2,1 (c) 1,1/2 (d) 0,1/2

Soln.

Bosons

$ 1\rangle$	$ 2\rangle$	$ 3\rangle$
••		
	••	
		••
•	•	
•		•
	•	•

$$\frac{P(\text{same})}{P(\text{different})} = \frac{3/6}{3/6} = 1$$

Classical particles

$ 1\rangle$	$ 2\rangle$	$ 3\rangle$
AB		
	AB	
		AB
A	B	
B	A	
A		B
B		A
	A	B
	B	A

$$\frac{P(\text{same})}{P(\text{different})} = \frac{3/9}{6/9} = \frac{1}{2}$$

Correct option is (c)

- Q. When a collection of two-level systems is in equilibrium at temperature T_0 , the ratio of the population in the lower and upper levels is 2 : 1. When the temperature is changed to T , the ratio is 8 : 1. Then

- (a) $T = 2T_0$ (b) $T_0 = 2T$ (c) $T_0 = 3T$ (d) $T_0 = 4T$ [JEST 2018]

Soln. If the energy levels are E_1 and E_2 , then

$$\frac{N_1}{N_2} = \frac{e^{-E_1/k_B T_0}}{e^{-E_2/k_B T_0}} = \frac{2}{1} \Rightarrow e^{(E_2 - E_1)/k_B T_0} = 2 \quad \dots (1)$$

When the ratio changes to 8 : 1, then

$$\frac{N_1}{N_2} = \frac{e^{-E_1/k_B T}}{e^{-E_2/k_B T}} = \frac{8}{1} \Rightarrow e^{(E_2 - E_1)/k_B T} = 8 \Rightarrow e^{(E_2 - E_1)/k_B T} = (2)^3 = e^{3(E_2 - E_1)/k_B T_0}$$

$$\Rightarrow \frac{1}{T} = \frac{3}{T_0} \Rightarrow T_0 = 3T$$

Correct option is (c)

- Q. For a system in thermal equilibrium with a heat bath at temperature T , which one of the following equalities is correct? [JEST 2015]

$$\left(\beta = \frac{1}{k_B T} \right)$$

$$(a) \frac{\partial}{\partial \beta} \langle E \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$(b) \frac{\partial}{\partial \beta} \langle E \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$(c) \frac{\partial}{\partial \beta} \langle E \rangle = \langle E^2 \rangle + \langle E \rangle^2$$

$$(d) \frac{\partial}{\partial \beta} \langle E \rangle = -(\langle E^2 \rangle + \langle E \rangle^2)$$



Soln. The average energy is

$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$\therefore \frac{\partial}{\partial \beta} \langle E \rangle = \frac{\left(\sum_i e^{-\beta E_i} \right) \left(-\sum_i E_i^2 e^{-\beta E_i} \right) + \left(\sum_i E_i e^{-\beta E_i} \right)^2}{\left(\sum_i e^{-\beta E_i} \right)^2}$$

$$= \langle E \rangle^2 - \langle E^2 \rangle.$$

Correct option is (a)

Q. If the mean square fluctuations in energy of a system in equilibrium at temperature T is proportional to T^α , then the energy of the system is proportional to **[JEST 2017]**

- (a) $T^{\alpha-2}$ (b) $T^{\alpha/2}$ (c) $T^{\alpha-1}$ (d) T^α

Soln. The mean square fluctuation $(\Delta E)^2$ and the average energy $\langle E \rangle$ is related as

$$(\Delta E)^2 = k_B T^2 \frac{\partial}{\partial T} \langle E \rangle,$$

where $(\Delta E)^2 = AT^\alpha$, where A is some proportionality constant.

$$\therefore \frac{\partial}{\partial T} \langle E \rangle = \frac{A}{k_B} T^{\alpha-2}$$

$$\therefore \langle E \rangle = \frac{A}{k_B} \int T^{\alpha-2} dT \propto T^{\alpha-1}$$

Correct option is (c)

Q. For a classical system of non-interacting particles in the presence of a spherically symmetric potential $V(r) = \gamma r^3$, what is the mean energy per particle? γ is a constant. **[JEST 2018]**

- (a) $\frac{3}{2} k_B T$ (b) $\frac{5}{2} k_B T$ (c) $\frac{3}{2} \gamma k_B T$ (d) $\frac{3}{2} \gamma k_B T$

Soln. The Hamiltonian is

$$H = \frac{p_r^2}{2m} + \gamma r^3 = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \gamma (x^2 + y^2 + z^2)^{3/2}$$

Using law of equipartition of energy

$$\left\langle x_n \frac{\partial H}{\partial x_n} \right\rangle = k_B T, \text{ we have}$$

$$\left\langle p_x \frac{\partial H}{\partial p_x} \right\rangle = \left\langle \frac{p_x^2}{m} \right\rangle = k_B T, \text{ or } \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{1}{2} k_B T$$

$$\text{Similarly, } \left\langle \frac{p_y^2}{2m} \right\rangle = \left\langle \frac{p_z^2}{2m} \right\rangle = \frac{1}{2} k_B T$$

$$\text{Also, } \left\langle x \frac{\partial H}{\partial x} \right\rangle + \left\langle y \frac{\partial H}{\partial y} \right\rangle + \left\langle z \frac{\partial H}{\partial z} \right\rangle = \left\langle 3\gamma (x^2 + y^2 + z^2)^{3/2} \right\rangle = 3k_B T$$



$$\Rightarrow \left\langle \gamma (x^2 + y^2 + z^2)^{3/2} \right\rangle = k_B T$$

$$\therefore \langle H \rangle = \frac{3}{2} k_B T + k_B T = \frac{5}{2} k_B T$$

Correct option is (b)

- Q. A monoatomic gas consists of atoms with two internal energy levels, ground state $E_0 = 0$ and an excited state $E_1 = E$. The specific heat of the gas is given by [JEST 2014]

(a) $\frac{3}{2} k$ (b) $\frac{E^2 e^{E/kT}}{kT^2 (1 + e^{E/kT})^2}$
 (c) $\frac{3}{2} k + \frac{E^2 e^{E/kT}}{kT^2 (1 + e^{E/kT})^2}$ (d) $\frac{3}{2} k - \frac{E^2 e^{E/kT}}{kT^2 (1 + e^{E/kT})^2}$

Soln. The average energy is

$$\langle E \rangle = \frac{E_1 e^{-E_1/kT} + E_2 e^{-E_2/kT}}{e^{-E_1/kT} + e^{-E_2/kT}} = \frac{E e^{-E/kT}}{1 + e^{-E/kT}} = \frac{E}{e^{E/kT} + 1}$$

$E_1 = E$ _____
 $E_0 = 0$ _____

Therefore, the total energy is

$$\langle E \rangle = \frac{3}{2} k_B T + \langle E' \rangle = \frac{3}{2} k_B T + \frac{E}{1 + e^{E/kT}}$$

The specific heat is given by

$$C_v = \frac{d}{dT} \langle E \rangle = \frac{3}{2} k_B + \frac{E^2}{kT^2} \frac{e^{E/kT}}{(1 + e^{E/kT})^2}$$

Correct option is (c)

- Q. A particle in thermal equilibrium has only 3 possible states with energies $-\varepsilon, 0, \varepsilon$. If the system is maintained at a temperature $T \gg \frac{\varepsilon}{k_B}$, then the average energy of the particle can be approximated to,

(a) $\frac{2\varepsilon^2}{3k_B T}$ (b) $-\frac{2\varepsilon^2}{3k_B T}$ (c) $-\frac{\varepsilon^2}{k_B T}$ (d) 0 [JEST 2015]

Soln. The average energy is given by

$$\langle E \rangle = \frac{\sum E_i e^{-E_i/k_B T}}{\sum e^{-E_i/k_B T}} = \frac{-\varepsilon e^{\varepsilon/k_B T} + \varepsilon e^{-\varepsilon/k_B T}}{e^{\varepsilon/k_B T} + 1 + e^{-\varepsilon/k_B T}}$$

_____ + ε
 _____ 0
 _____ - ε

When $T \gg \frac{\varepsilon}{k_B}$ or $\frac{\varepsilon}{k_B T} \ll 1$, we have

$$\langle E \rangle = \frac{-\varepsilon \left(1 + \frac{\varepsilon}{k_B T}\right) + \varepsilon \left(1 - \frac{\varepsilon}{k_B T}\right)}{\left(1 + \frac{\varepsilon}{k_B T}\right) + 1 + \left(1 - \frac{\varepsilon}{k_B T}\right)} = -\frac{2\varepsilon^2}{3} = -\frac{2\varepsilon^2}{3k_B T^2}$$

Correct option is (b)



Q. A collection of N two-level systems with energies 0 and $E > 0$ is in thermal equilibrium at temperatures T . For $T \rightarrow \infty$, the specific heat approaches. [JEST 2012]

- (a) 0 (b) Nk_B (c) $3Nk_B/2$ (d) ∞

Soln. The average energy is

$$\langle E \rangle = \frac{NE e^{-E/k_B T}}{1 + e^{-E/k_B T}} \quad \begin{array}{l} \text{————— } E \\ \text{————— } 0 \end{array}$$

The specific heat is given by

$$C = \frac{d}{dT} \langle E \rangle = \frac{NE^2}{k_B T^2} \frac{e^{E/k_B T}}{(1 + e^{E/k_B T})^2}$$

When $T \rightarrow \infty$, $e^{E/k_B T} \approx 1$ and $\frac{1}{T} \rightarrow 0$.

Therefore, $C = 0$.

Correct option is (a)

Q. Consider a particle with three possible spin states; $s = 0$ and ± 1 . There is a magnetic field h present and the energy for a spin state s is $-hs$. The system is at a temperature T . Which of the following statements is true about the entropy $S(T)$? [JEST 2013]

- (a) $S(T) = \ln 3$ at $T = 0$, and 3 at high T (b) $S(T) = \ln 3$ at $T = 0$, and zero at high T
(c) $S(T) = 0$ at $T = 0$, and 3 at high T (d) $S(T) = 0$ for $T = 0$, and $\ln 3$ at high T

Soln. The energies are

$$E = \begin{cases} +hs & , s = -1 \\ 0 & , s = 0 \\ -hs & , s = 1 \end{cases}$$

So the partition function is

$$Z = e^{-hs/k_B T} + 1 + e^{hs/k_B T}$$

The free energy is

$$F = -k_B T \ln Z = -k_B T \ln \left(1 + e^{-\frac{hs}{k_B T}} + e^{\frac{hs}{k_B T}} \right)$$

The entropy is given by $S = -\left(\frac{\partial F}{\partial T}\right)_V$

$$\begin{aligned} \Rightarrow S &= k_B \ln \left(1 + e^{-\frac{hs}{k_B T}} + e^{\frac{hs}{k_B T}} \right) + k_B T \frac{\frac{hs}{k_B T^2} e^{-\frac{hs}{k_B T}} - \frac{hs}{k_B T^2} e^{\frac{hs}{k_B T}}}{1 + e^{-\frac{hs}{k_B T}} + e^{\frac{hs}{k_B T}}} \\ &= k_B \ln \left(1 + e^{-\frac{hs}{k_B T}} + e^{\frac{hs}{k_B T}} \right) + \frac{hs}{T} \frac{e^{-\frac{hs}{k_B T}} - e^{\frac{hs}{k_B T}}}{1 + e^{-\frac{hs}{k_B T}} + e^{\frac{hs}{k_B T}}} \end{aligned}$$

At low temperature, $e^{-\frac{hs}{k_B T}}$ is very small and $e^{\frac{hs}{k_B T}}$ is very large.

$$\therefore S = k_B \ln \left(e^{\frac{hs}{k_B T}} \right) + \frac{hs}{T} \left(-\frac{e^{\frac{hs}{k_B T}}}{e^{\frac{hs}{k_B T}}} \right)$$



$$= k_B \left(\frac{hs}{k_B T} \right) - \frac{hs}{T} = 0.$$

At high temperature, $e^{-\frac{hs}{k_B T}}$ and $e^{\frac{hs}{k_B T}}$ both tends to unity.

$$\therefore S = k_B \ln(3).$$

Correct option is (d)

- Q.** Consider a system of $2N$ non-interacting spin $1/2$ particles each fixed in position and carrying a magnetic moment μ . The system is immersed in a uniform magnetic field B . The number of spin up particle for which the entropy of the system will be maximum is **[JEST 2014]**

- (a) 0 (b) N (c) $2N$ (d) $N/2$

Soln. Let N_1 and N_2 be the number of particles with spin up and spin down respectively. Then,

$$N_1 + N_2 = 2N.$$

Therefore, thermodynamic probability for having N_1 spins up is

$$\Omega = {}^{2N}C_{N_1} = \frac{(2N)!}{N_1!(2N - N_1)!}$$

$$\therefore S = k_B \ln \Omega = k_B \ln \left[\frac{(2N)!}{N_1!(2N - N_1)!} \right]$$

Using Stirling's approximation, $\ln x! = x \ln x - x$ (for large x)

$$\text{Thus, } S = k_B [(2N \ln 2N - 2N) - (N_1 \ln N_1 - N_1) - \{(2N - N_1) \ln (2N - N_1) - (2N - N_1)\}]$$

For maximum entropy, we have

$$\frac{dS}{dN_1} = 0.$$

$$\text{Thus, } -(1 + \ln N_1 - 1) - [-1 - \ln (2N - N_1) + 1] = 0$$

$$\Rightarrow \ln \left(\frac{2N - N_1}{N_1} \right) = 0 \quad \Rightarrow N_1 = N.$$

Correct option is (b)

- Q.** A collection of N interacting magnetic moments, each of magnitude μ , is subjected to a magnetic field H along the z -direction. Each magnetic moment has a doubly degenerate level of energy zero, and two non-degenerate levels of energies $-\mu H$ and μH respectively. The collection is in thermal equilibrium at temperature T . The total energy $E(T, H)$ of the collection is **[JEST 2018]**

$$(a) \frac{\mu H N \sinh(\mu H / k_B T)}{1 + \cosh(\mu H / k_B T)}$$

$$(b) -\frac{\mu H N}{2(1 + \cosh(\mu H / k_B T))}$$

$$(c) -\frac{\mu H N \cosh(\mu H / k_B T)}{1 + \cosh(\mu H / k_B T)}$$

$$(d) -\mu H N \frac{\sinh(\mu H / k_B T)}{\cosh(\mu H / k_B T)}$$

Soln. The given energy levels are

$$E = \begin{cases} -\mu H & (\text{degeneracy} = 1) \\ 0 & (\text{degeneracy} = 2) \\ +\mu H & (\text{degeneracy} = 1) \end{cases}$$



The total energy is,

$$\begin{aligned}
 \langle E \rangle &= N \frac{\left[-1\mu H e^{\frac{\mu H}{k_B T}} + 2.0 e^{-0/k_B T} + 1 \cdot \mu H e^{-\mu H/k_B T} \right]}{\left[1 \cdot e^{\mu H/k_B T} + 2 \cdot e^{-0/k_B T} + 1 \cdot e^{-\mu H/k_B T} \right]} \\
 &= \frac{-N\mu H \left[e^{\mu H/k_B T} - e^{-\mu H/k_B T} \right]}{\left[2 + e^{\mu H/k_B T} + e^{-\mu H/k_B T} \right]} = \frac{-\mu H N \sinh(\mu H / k_B T)}{\left[2 + 2 \cosh(\mu H / k_B T) \right]} \\
 &= -\frac{\mu H N \sinh(\mu H / k_B T)}{1 + \cosh(\mu H / k_B T)}
 \end{aligned}$$

Correct option is (a)

- Q. A two dimensional box in a uniform magnetic field B contains $N/2$ localised spin- $\frac{1}{2}$ particles with magnetic moment μ , and $N/2$ free spinless particles which do not interact with each other. The average energy of the system at a temperature T is : [JEST 2016]

- (a) $3NkT - \frac{1}{2}N\mu B \sinh(\mu B/k_B T)$ (b) $NkT - \frac{1}{2}N\mu B \tanh(\mu B/k_B T)$
 (c) $\frac{1}{2}NkT - \frac{1}{2}N\mu B \tanh(\mu B/k_B T)$ (d) $\frac{3}{2}NkT + \frac{1}{2}N\mu B \cosh(\mu B/k_B T)$

Soln. The average energy of $N/2$ free spinless particles is

$$\langle E_1 \rangle = \frac{N}{2} \times \frac{2}{2} k_B T = Nk_B T$$

and of $N/2$ localised spin- $\frac{1}{2}$ particles is

$$\langle E_2 \rangle = -\frac{N}{2} \mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$

\therefore The average energy of the system is

$$\begin{aligned}
 \langle E \rangle &= \langle E_1 \rangle + \langle E_2 \rangle \\
 &= Nk_B T - \frac{N}{2} \mu B \tanh\left(\frac{\mu B}{k_B T}\right)
 \end{aligned}$$

Correct option is (b)

- Q. For a quantum mechanical harmonic oscillator with energies, $E_n = (n + 1/2)\hbar\omega$, where $n = 0, 1, 2, \dots$, the partition function is:

- (a) $\frac{e^{\hbar\omega/k_B T}}{e^{\hbar\omega/k_B T} - 1}$ (b) $e^{\hbar\omega/2k_B T} - 1$ (c) $e^{\hbar\omega/2k_B T} + 1$ (d) $\frac{e^{\hbar\omega/2k_B T}}{e^{\hbar\omega/k_B T} - 1}$ [JEST 2016]

Soln. $Z_1 = \sum_n g_n e^{-E_n/k_B T}$

$$= \sum_n e^{-\left(n + \frac{1}{2}\right) \frac{\hbar\omega}{k_B T}}, \text{ where } g_n = 1 \text{ for all values of } n$$



$$= e^{\frac{h\omega}{k_B T}} \sum_n e^{-n \frac{h\omega}{k_B T}} = \frac{e^{-h\omega/2k_B T}}{1 - e^{-h\omega/2k_B T}}$$

Correct option is (d)

- Q.** A system of particles of N lattice sites is in equilibrium at temperature T and chemical potential μ . Multiple occupancy of the sites is forbidden. The binding energy of a particle at each site is $-\epsilon$. The probability of on site being occupied is [JEST 2017]

(a) $\frac{1 - e^{\beta(\mu + \epsilon)}}{1 - e^{-(N+1)\beta(\mu + \epsilon)}}$ (b) $\frac{1}{[1 + e^{\beta(\mu + \epsilon)}]^N}$ (c) $\frac{1}{[1 + e^{-\beta(\mu + \epsilon)}]^N}$ (d) $\frac{1 - e^{-\beta(\mu + \epsilon)}}{1 - e^{-(N+1)\beta(\mu + \epsilon)}}$

Soln. The probability of occupying a site is

$$P_1 = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} = \frac{1}{e^{-\beta(\epsilon + \mu)} + 1} = \frac{e^{\beta(\epsilon + \mu)}}{1 + e^{\beta(\epsilon + \mu)}}$$

The probability of not occupying a site is

$$\bar{P}_1 = 1 - P_1 = \frac{1}{1 + e^{\beta(\epsilon + \mu)}}$$

$$\text{Required probability} = \left[\frac{1}{1 + e^{\beta(\epsilon + \mu)}} \right]^N$$

Correct option is (b)

- Q.** Two classical particles are distributed among $N (> 2)$ sites on a ring. Each site can accommodate only one particle. If two particles occupy two nearest neighbour sites, then the energy of the system is increased by ϵ . The average energy of the system at temperature T is [JEST 2017]

(a) $\frac{2\epsilon e^{-\beta\epsilon}}{(N-3) + 2e^{-\beta\epsilon}}$ (c) $\frac{2N\epsilon e^{-\beta\epsilon}}{(N-3) + 2e^{-\beta\epsilon}}$ (c) $\frac{\epsilon}{N}$ (d) $\frac{2\epsilon e^{-\beta\epsilon}}{(N-2) + 2e^{-\beta\epsilon}}$

Soln. Total number of possible microstates to arrange two particles = $N(N-1)$

Total number of microstates when two particles are neighbour = $2N$

\therefore Total number of microstates when two particles are not neighbour of each other

$$= N(N-1) - 2N = N^2 - 3N$$

$$\therefore \langle E \rangle = \frac{2N\epsilon e^{-\beta\epsilon}}{2Ne^{-\beta\epsilon} + N(N-3)e^{-\beta \cdot 0}}$$

$$= \frac{2\epsilon e^{-\beta\epsilon}}{2e^{-\beta\epsilon} + (N-3)}$$

Correct option is (a)

- Q.** Consider a system of particles in three dimension with momentum \vec{p} and energy $E = c|\vec{p}|$, c being a constant. The system is maintained at inverse temperature β , volume V and chemical potential μ . What is the grand partition function of the system? [JEST 2012]

(a) $\exp \left[e^{\beta\mu} 8\pi V / (\beta c h)^3 \right]$

(b) $e^{\beta\mu} 6\pi V / (\beta c h)^2$



$$(c) \exp \left[e^{\beta \mu} 6\pi V / (\beta c h)^3 \right]$$

$$(d) e^{\beta \mu} 8\pi V / (\beta c h)^2$$

Soln. We have,

$$Z_1(V, T) = \frac{1}{h^3} \int d\vec{r} \int d\vec{p} e^{-\beta E} = \frac{V}{h^3} \int e^{-\beta c |\vec{p}|} d\vec{p} = \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z e^{-\beta c \sqrt{p_x^2 + p_y^2 + p_z^2}}$$

Using spherical polar coordinate, we have

$$= \frac{4\pi V}{h^3} \int_0^{\infty} r^2 e^{-\beta c r} dr = \frac{8\pi V}{(\beta c h)^3}$$

Therefore, the grand partition function is

$$\begin{aligned} Z &= \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{(z(V, T))^N}{N!} \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{8\pi V}{(\beta c h)^3} e^{\beta \mu} \right]^N \\ &= \exp \left[\frac{e^{\beta \mu} 8\pi V}{(\beta c h)^3} \right] \end{aligned}$$

Correct option is (a)

- Q. Consider a system maintained at temperature T , with two available energy states E_1 and E_2 each with degeneracies g_1 and g_2 . If p_1 and p_2 are probabilities of occupancy of the two energy states, what is the entropy of the system? [JEST 2012]

$$\begin{aligned} (a) S &= -k_B [p_1 \ln(p_1/g_1) + p_2 \ln(p_2/g_2)] & (b) S &= -k_B [p_1 \ln(p_1 g_1) + p_2 \ln(p_2 g_2)] \\ (c) S &= -k_B [p_1 \ln(p_1^{g_1}) + p_2 \ln(p_2^{g_2})] & (d) S &= -k_B [(1/p_1) \ln(p_1/g_1) + (1/p_2) \ln(p_2/g_2)] \end{aligned}$$

Soln. If N_1 and N_2 be the average number of particles in the level with energy E_1 and E_2 respectively. Then,

The number of microstates are

$$\Omega = N! \frac{\prod g_i^{N_i}}{\prod N_i!}, \text{ where } N = \sum_i N_i$$

$$\text{Therefore, } S = k_B \ln \Omega = k_B [\ln N! + N_1 \ln g_1 + N_2 \ln g_2 - \ln N_1! - \ln N_2!]$$

Using Stirling's approximation, $\ln x! = x \ln x - x$ (for large x), we have

$$S = k_B [N \ln N - N_1 \ln N_1 - N_2 \ln N_2 + N_1 \ln g_1 + N_2 \ln g_2],$$

$$\text{where by definition } p_1 = \frac{N_1}{N} \text{ and } p_2 = \frac{N_2}{N}$$

$$\text{Therefore, } S = k_B [N \ln N - N p_1 \ln N p_1 - N p_2 \ln N p_2 + N p_1 \ln p_1 + N p_2 \ln g_2]$$

$$= k_B \left[N \ln N + N p_1 \ln \frac{g_1}{N p_1} + N p_2 \ln \frac{g_2}{N p_2} \right]$$

$$\text{For } N=1, \text{ we have } S = -k_B [p_1 \ln(p_1/g_1) + p_2 \ln(p_2/g_2)].$$

Correct option is (a)

Chapter 7

Distribution laws of classical & quantum statistical physics

The Boundary between classical and quantum regime

Mean thermal wavelength or mean thermal de-Broglie wavelength.

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Degeneracy discriminant factor:

$$n\lambda^3 = \frac{N}{V} \frac{h^3}{(2\pi m k_B T)^{3/2}}$$

(i) If $n\lambda^3 \ll 1$ for classical consideration or non-degenerate case

$$\lambda \ll \left(\frac{V}{N}\right)^{1/3} \rightarrow \text{Mean equilibrium separation}$$

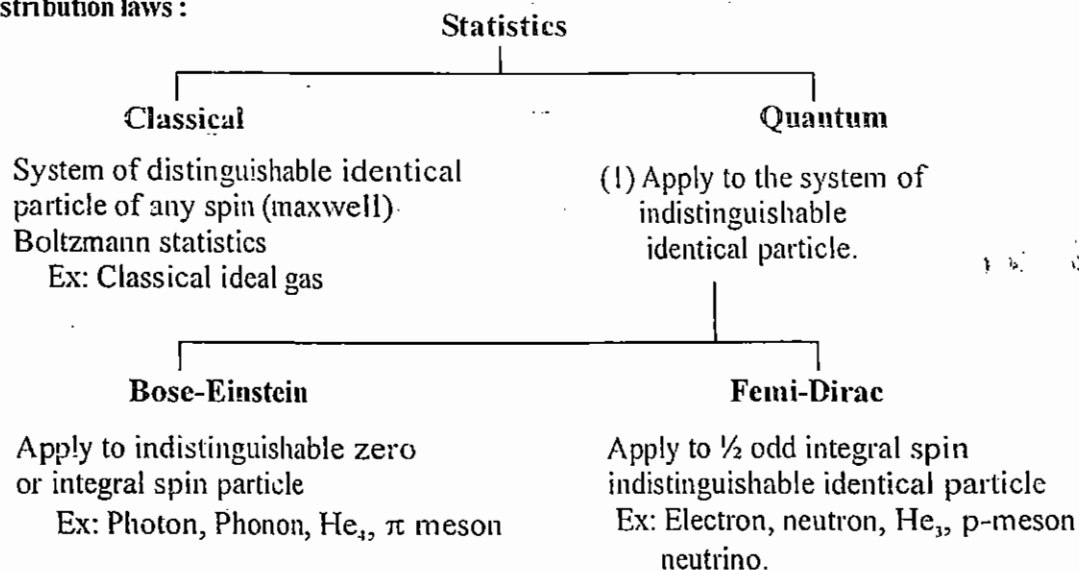
(ii) If $n\lambda^3$ is small but non equal to zero departure. This sets for classical behaviour.

(iii) If $n\lambda^3 \approx 1$ for quantum consideration

(iv) If $n\lambda^3 \gg 1$ for strongly degenerate case

(v) If $n\lambda^3 \rightarrow \infty$ complete degenerate.

Distribution laws :





Maxwell - Boltzmann : The number of distinct ways (microstate) associated with i th cell in Maxwell Boltzmann Statistics is

$$(\omega)_{M-B} (i) = (g_i)^{n_i}$$

$$W_{M-B} (i) = N! \prod_i \frac{(g_i)^{n_i}}{n_i!} \quad (\text{for distinguishable particles}) \quad \dots (1)$$

$$= \prod_i \frac{(g_i)^{n_i}}{n_i!} \quad (\text{for indistinguishable particles}) \quad \dots (2)$$

Bose- Einstein:
$$\omega_{BE} = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots (3)$$

Fermi-Dirac:
$$\omega_{FD} (i) = \frac{g_i!}{n_i! (g_i - n_i)!} \Rightarrow W_{FD} (i) = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \quad \dots (4)$$

To determine most probable distribution function, we use Lagrangian undetermined multiplier method.

Bose Einstein distribution function :

$$\text{We have } \sum n_i = N \Rightarrow \sum \delta n_i = 0 \text{ and } \sum \epsilon_i n_i = E \Rightarrow \sum \epsilon_i \delta n_i = 0$$

$$\text{Now, } W = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$\begin{aligned} \ell n W &= \sum_i (\ell n (n_i + g_i - 1)! - \ell n n_i! - \ell n (g_i - 1)!) \\ &= \sum_i (\ell n (n_i + g_i)! - \ell n n_i! - \ell n g_i!) \quad (\text{for } n_i \gg 1) \\ &= \sum_i ((n_i + g_i) \ell n (n_i + g_i) - n_i \ell n n_i - g_i \ell n g_i) \end{aligned}$$

where we have used Stirling's approximation

$$\text{So, } \ell n W = \sum_i ((n_i + g_i) \ell n (n_i + g_i) - n_i \ell n n_i - g_i \ell n g_i)$$

$$\begin{aligned} \text{So, } \delta \ell n W &= \sum_i (n_i + g_i) \frac{1}{n_i + g_i} \delta n_i + \delta n_i \ell n (n_i + g_i) - n_i \times \frac{\delta n_i}{n_i} - \ell n n_i \times \delta n_i \\ &= \sum_i \ell n \left(\frac{n_i + g_i}{n_i} \right) \delta n_i \end{aligned}$$

$$\text{By using the Lagrange undetermined multiplier method } \delta \ell n W - \alpha \sum_i \delta n_i - \beta \sum_i \epsilon_i \delta n_i = 0$$

For most probable state $\delta \ell n W = 0$

$$\sum_i \left[\ell n \frac{n_i + g_i}{n_i} - \alpha - \beta \epsilon_i \right] \delta n_i = 0$$

For being true for every value of i , we have

$$\ell n \frac{n_i + g_i}{n_i} - \alpha - \beta \epsilon_i = 0 \Rightarrow \frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} - 1$$



$$\Rightarrow \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1} = f_{B-E} \quad \dots (1)$$

Equation (1) represent the mean occupation no. for a level of energy ϵ_i or probability of occupation or most probable distribution function or average of particle per level for i th cell. Similarly,

$$f_{MB} = \frac{1}{e^{\alpha + \beta \epsilon_i}}$$

$$f_{FD} = \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$$

In general $f = \frac{1}{e^{\alpha + \beta \epsilon_i} + a}$ where,

$$a = 0 \quad \text{for M.B}$$

$$a = 1 \quad \text{for F.D}$$

$$a = -1 \quad \text{for B.E}$$

Grand canonical partition function for F.D. (Fermi-Dirac distribution), B.E. (Bose-Einstein distribution) and M.B. (Maxwell-Boltzmann distribution).

Single state grand canonical partition function for F.D.:

$$\sum_{N_r} e^{-\alpha N_r - \beta E_s} = 1 + e^{\frac{\mu}{k_B T} - \frac{\epsilon_s}{k_B T}} = 1 + e^{\frac{\mu - \epsilon_s}{k_B T}}$$

Total grand canonical partition function for F.D.

$$Z(\mu, V, T) = \prod_s \left(1 + e^{\frac{\mu - \epsilon_s}{k_B T}} \right)$$

Single state grand canonical partition function for B.E

$$\sum_{N_r} e^{-\alpha N_r - \beta E_s} = 1 + e^{\frac{\mu - \epsilon_s}{k_B T}} + e^{\frac{2(\mu - \epsilon_s)}{k_B T}} + e^{\frac{3(\mu - \epsilon_s)}{k_B T}} + \dots$$

Total grand canonical partition function for B.E

$$Z(\mu, V, T) = \prod_s \left(1 - e^{\frac{\mu - \epsilon_s}{k_B T}} \right)^{-1} = \prod_s \left(1 - Z e^{-\beta \epsilon_s} \right)^{-1}$$

If $Z e^{-\beta \epsilon_s} \gg 1$ then the series is infinite so $Z e^{-\beta \epsilon_s} > 1$

$$Z(\mu, V, T) = \prod_s \left(1 + Z e^{\beta \epsilon_s} \right)$$

Single state grand canonical P.F. (Partition Function) for M.B

$$= \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V, T) \sum_{N_r=0}^{\infty} \frac{z^{N_r} V^N}{N! \lambda^{3N}} = \exp \frac{zV}{\lambda^3} \rightarrow \text{for indistinguishable}$$

$$= \sum_{N_r=0}^{\infty} \frac{z^{N_r} V^N}{\lambda^{3N}} \rightarrow \text{for distinguishable case}$$

$$S = -k_B \sum_{r,s} P_{rs} \ln P_{rs}$$



$$P_{r,s} = c \frac{e^{\mu N_r - \beta E_s}}{k_B T} / Z(z, V, T)$$

$$S = -k_B \sum_{r,s} \frac{e^{\mu N_r - \beta E_s}}{Z(z, V, T)} \left[(\mu N_r - E_s) \beta - \ln Z(z, V, T) \right]$$

$$= -k_B \left[\sum_{r,s} \mu N_r \frac{e^{\mu N_r - \beta E_s}}{Z(z, V, T)} - \sum_{r,s} \frac{\beta E_s e^{\mu N_r - \beta E_s}}{Z(z, V, T)} - \sum_{r,s} \frac{e^{\mu N_r - \beta E_s}}{Z(z, V, T)} \ln Z(z, V, T) \right]$$

$$\text{But } \sum_{r,s} e^{\mu N_r - \beta E_s} = Z(z, V, T)$$

$$S = -k_B \left[\mu \beta \bar{N} - \beta \bar{E} - \ln Z(z, V, T) \right] = -\mu k_B \beta \bar{N} + k_B \beta \bar{E} + k_B \ln Z(z, V, T)$$

$$= -\frac{\mu \bar{N}}{T} + \frac{U}{T} + k_B \ln Z(z, V, T)$$

The Grand canonical potential is defined as

$$\Omega = U - TS - \mu \bar{N}$$

Comparing (x) and (xx) we get

$$\Omega = -k_B T \ln Z(z, V, T)$$

$$\text{Now } d\Omega = -SdT - \bar{N}d\mu - PdV$$

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{\mu, V} \quad \bar{N} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} \quad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu}$$

Ideal Bose-Einstein Gas

Consider a B.E gas of N atoms. Let these particle be distributed among states such that there are n_1, n_2, \dots, n_i number of particle in quantum state whose energies are $\epsilon_1, \epsilon_2, \dots, \epsilon_i$ respectively.

The most probable distribution function for B.E gas

$$f_{BE}(\epsilon_i) = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}$$

Let the interaction between the particle is assumed to be negligible so that the energy may be regarded entirely of translational character. As translational levels are closely spaced, so we will represent the summation by integration

$$g(\epsilon) d\epsilon = g_s \frac{2\pi V (2m)^{3/2}}{h^3} \epsilon^{1/2} d\epsilon$$

$g_s = (2S+1)$ is the spin degeneracy factor

The number of particle having energy between ϵ and $\epsilon + d\epsilon$

$$N(\epsilon) d\epsilon = f(\epsilon) g(\epsilon) d\epsilon = \frac{g_s \frac{2\pi V (2m)^{3/2}}{h^3} \epsilon^{1/2}}{e^{\alpha + \beta \epsilon} - 1} d\epsilon$$

Total number of particle in the system



$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\alpha} e^{\beta\epsilon} - 1} \quad \dots (1)$$

Now,

$$\Omega = -k_B T \ln Z (\mu, V, T).$$

$$\Omega = -k_B T \ln \prod_s (1 - e^{-\alpha} e^{-\beta E_s}) = -k_B T \sum_s \ln (1 - e^{-\alpha} e^{-\beta E_s})$$

$$= -k_B T \frac{2\pi g_s V (2m)^{3/2}}{h^3} \int \epsilon^{1/2} \ln (1 - e^{-\alpha} e^{-\beta\epsilon}) d\epsilon$$

$$= -k_B T \frac{2\pi g_s V (2m)^{3/2}}{h^3} \left[\ln (1 - e^{-\alpha} e^{-\beta\epsilon}) \frac{\epsilon^{3/2}}{\frac{3}{2}} \right]_0^\infty - \int \frac{-e^{-\alpha} e^{-\beta\epsilon}}{1 - e^{-\alpha} e^{-\beta\epsilon}} \times \beta \epsilon^{3/2} \times \frac{2}{3} d\epsilon$$

$$\Omega = -\frac{2}{3} \frac{2\pi g_s V (2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\alpha+\beta\epsilon} - 1} d\epsilon \quad \dots (2)$$

$$\text{Also, } U = \int \epsilon N(\epsilon) d\epsilon = 2\pi g_s V (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\alpha+\beta\epsilon} - 1} d\epsilon \quad \dots (3)$$

Comparing equations (2) and (3)

$$\Omega = -\frac{2}{3} U = -PV \Rightarrow \boxed{PV = \frac{2}{3} U}$$

$$U = 2\pi g_s V \frac{(2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\alpha+\beta\epsilon} - 1} d\epsilon$$

$$\text{Let } \frac{\epsilon}{k_B T} = x \Rightarrow d\epsilon = k_B T dx$$

$$U = \frac{2\pi g_s V (2mk_B T)^{3/2}}{h^3} k_B T \int_0^\infty \frac{x^{3/2}}{e^{\alpha} e^x - 1} dx$$

$$\text{Now } \int_0^\infty \frac{x^{3/2}}{e^{\alpha} e^x - 1} dx = \int_0^\infty \frac{x^{3/2} e^{-x}}{e^{\alpha} \left(1 - \frac{e^{-x}}{e^{\alpha}}\right)} dx \quad \{\because (1-x)^{-1} = 1+x+x^2; x \ll 1\}$$

$$\int_0^\infty x^{3/2} \frac{e^{-x}}{e^{\alpha}} \left(1 + \frac{e^{-x}}{e^{\alpha}} + \frac{e^{-2x}}{e^{2\alpha}} + \dots\right) dx = \int_0^\infty x^{3/2} \frac{e^{-x}}{e^{\alpha}} dx + \int_0^\infty x^{3/2} \frac{e^{-2x}}{e^{2\alpha}} dx + \int_0^\infty x^{3/2} \frac{e^{-3x}}{e^{3\alpha}} dx + \dots$$

$$(\text{Formula } \int_0^\infty e^{-ax} x^n = \frac{\Gamma(n+1)}{a^{n+1}})$$



$$= \frac{1}{e^\alpha} \frac{\Gamma\left(\frac{5}{2}\right)}{1^2} + \frac{1}{e^{2\alpha}} \frac{\Gamma\left(\frac{5}{2}\right)}{2^2} + \frac{1}{e^{3\alpha}} \frac{\Gamma\left(\frac{5}{2}\right)}{3^2} + \dots$$

$$= \frac{3}{4} \sqrt{\pi} \left(\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \dots \right)$$

$$\text{Now } U = \frac{2g_s V}{\sqrt{\pi}} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} k_B T \int_0^\infty \frac{x^{3/2}}{e^\alpha e^x - 1} dx$$

$$U = \frac{2g_s}{\sqrt{\pi}} Z_1 k_B T \times \frac{3}{4} \sqrt{\pi} \left[\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \dots \right] \quad \left(\text{where, } Z_1 = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right)$$

$$= \frac{3}{2} g_s Z_1 k_B T \left[\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \dots \right]$$

From equation (1),

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^\infty \frac{e^{1/2} dE}{e^\alpha e^{\beta E} - 1} = g_s Z_1 \left[\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \dots \right]$$

$$U = \frac{3}{2} N k_B T \left[\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \dots \right] \left[\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \dots \right]^{-1}$$

Now,

$$U = \frac{3}{2} N k_B T \left[1 - \frac{1}{e^\alpha 2^{5/2}} + \frac{1}{e^{2\alpha} 3^{5/2}} + \dots \right] \left[1 - \frac{1}{e^\alpha 2^{5/2}} - \frac{1}{e^{2\alpha} 3^{5/2}} + \dots \right]$$

$$= \frac{3}{2} N k_B T \left[1 - \frac{1}{e^\alpha 2^{5/2}} - \frac{1}{e^{2\alpha} 3^{5/2}} + \dots \right]$$

So we are not obtaining the U as in classical ideal gas. Its value will decrease by some factor.

$$\Omega = -k_B T \ln Z(z, V, T) = \frac{2}{3} U = -PV$$

$$\Omega = U = TS - \mu \bar{N} = U - TS - G = U - TS - A - PV = -PV$$

$$P = \frac{2}{3} \frac{U}{V} \quad \dots (1)$$

This is same as in case of ideal gas

$$P = \frac{2}{3} \frac{U}{V} = \frac{N k_B T}{V} \left[1 - \frac{1}{e^\alpha 2^{5/2}} - \frac{1}{e^{2\alpha} 3^{5/2}} + \dots \right] \quad \dots (2)$$

From eqn (1) and (2) it is clear that there are deviation in energy and pressure from the values of classical ideal gas. The deviation from the perfect gas behaviour executed by B.E gas is termed as degeneracy. Comparing (1) and (2)



$$\frac{1}{e^{\alpha}} = \frac{n}{g_s} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} = \frac{N \lambda^3}{V g_s} \text{ -- degeneracy}$$

discriminant factor

Q. Free energy of a photon gas enclosed in a volume V is given by $F = -\frac{1}{3} a V T^4$, where a is the constant and T is the temperature of the gas. Find the chemical potential of the photon gas.

Soln. $F = U - TS$

$$dF = dU - TdS - SdT$$

$$dF = dU - PdV + \mu dN - SdT$$

$$= -SdT - PdV + \mu dN$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \frac{\partial}{\partial N} \left(-\frac{1}{3} a V T^4 \right) = 0.$$

Strong degenerate Boson gas (Bose-Einstein Condensation)

Chemical potential for Boson gas is always negative. The average no. of particle in the s^{th} particle state of

$$\text{energy } \epsilon_s \text{ is given by } f(\epsilon_s) = \frac{1}{e^{\frac{\epsilon_s - \mu}{k_B T}} - 1}$$

As the total no. of particles in Boson gas is fixed. So μ must increase as T decrease keeping volume constant, to keep $f(\epsilon_s)$ +ve consequently $\mu \rightarrow 0$. The no. of particle in ground state increases sharply. This macroscopic occupation of the ground state is called Bose-Einstein condensation. At very low temperature the value of μ is very close to the ground state energy i.e zero

At $T = T_B$

$$\frac{N}{V} = \frac{2\pi g_s (2mk_B T)^{3/2}}{h^3} \int_0^\infty \frac{x^{1/2} dx}{e^{\alpha} e^{x-1}}$$

$$\int_0^\infty \frac{x^{1/2} dx}{e^{x-1}} = \frac{\sqrt{\pi}}{2} \left[1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots \right] = \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right) \quad \left(\zeta\left(\frac{3}{2}\right) = 2.612 \right)$$

$$\frac{N}{V} = \frac{2\pi g_s}{h^3} (2mk_B T_B)^{3/2} \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right) = g_s \left(\frac{2\pi mk_B T_B}{h^2} \right)^{3/2} \zeta\left(\frac{3}{2}\right)$$

$$T_B = \frac{h^2}{2\pi m k_B} \left[\frac{N}{V g_s \zeta\left(\frac{3}{2}\right)} \right]^{2/3} \Rightarrow T_B = 0.084 \frac{h^2}{m k_B} \left[\frac{N}{V g_s} \right]^{2/3}$$

This is called condensation temperature, degeneracy temperature or characteristic temperature or Bose temperature or transition temperature. The condition for onset of Bose-Einstein gas (starting) is

$$N > V T^{3/2} \left(\frac{2\pi m k_B T}{h^3} \right)^{3/2} \zeta\left(\frac{3}{2}\right)$$

$$N = N_0 + N_e$$



$N_0 \rightarrow$ number of particle in the ground state

$N_e \rightarrow$ no of particle distributed over excited state

$$N_e = N \left(\frac{T}{T_B} \right)^{3/2}$$

$$N_0 = N - N_e = N \left[1 - \left(\frac{T}{T_B} \right)^{3/2} \right]$$

At $T < T_B$ the system may be looked upon as a mixture of two phase

(i) Normal phase consisting N_e particle distributed over excited state ($\epsilon \neq 0$)

(ii) Condensed phase consisting of no particle accumulated in the ground state ($\epsilon = 0$)

$$U = \frac{3}{2} N_e k_B T \frac{\xi\left(\frac{5}{2}\right)}{\xi\left(\frac{3}{2}\right)}$$

$$= \frac{3}{2} N \left(\frac{T}{T_B} \right)^{3/2} k_B T \frac{\xi\left(\frac{5}{2}\right)}{\xi\left(\frac{3}{2}\right)}$$

$$U = \frac{3}{2} N k_B T \left(\frac{T}{T_B} \right)^{3/2} \frac{1.342}{2.612}$$

$$= 0.5314 \times \frac{3}{2} N k_B T \left(\frac{T}{T_B} \right)^{3/2}$$

$$PV = \frac{2}{3} U = 0.53 N k_B T \left(\frac{T}{T_B} \right)^{3/2}$$

$$PV = 21.1 \text{ g}_s \frac{m^{3/2}}{h^3} (k_B T)^{5/2}$$

$P \propto T^{5/2}$ but independent of r and V only for $T < T_B$

The Bose - Einstein condensation take place in momentum space.

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 1.925 N k_B \left(\frac{T}{T_B} \right)^{3/2}$$

$$N\mu = U - TS + PV$$

$$\text{At } T < T_B, \mu = 0$$

$$S = \frac{PV + U}{T} = \frac{5}{2} \frac{PV}{T}$$

$$S = \frac{5}{2} \times 0.51 N k_B T \left(\frac{T}{T_B} \right)^{3/2} \Rightarrow S = N_e \frac{5}{2} \times 0.51 k_B$$

$$S \propto N_e, S \propto \left(\frac{T}{T_B} \right)^{3/2}$$



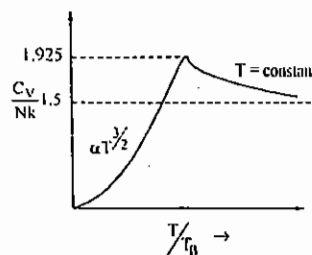
At $T = T_B$ all the thermodynamic quantities

P, U, S, A, Ω and C_V are continuous but derivative of specific heat is discontinuous at $T = T_B$

As $T \rightarrow \infty$ all the thermodynamic value approach to their classical value

$$PV^{5/3} = \text{constant}, \quad VT^{3/2} = \text{constant}$$

$$\frac{P}{T^{5/2}} = \text{constant}, \quad \gamma = \frac{C_P}{C_V}$$



This result is valid for Ideal Bose gas for reversible adiabatic process as for classical ideal gas but for ideal Bose

gas $\frac{C_P}{C_V} = \gamma \neq \frac{5}{3}$ always. At $T \gg T_B$ $\frac{C_P}{C_V} = \gamma = \frac{5}{3}$ but at any finite temperature γ is always greater than $\frac{5}{3}$.

Ideal Fermi Gas

Ideal Fermi gas

$0 < z < \infty$ – Ideal fermi gas

$0 < z < 1 \rightarrow$ – Ideal Bose gas $z = \text{fugacity}$

$$P = \frac{2}{3} \frac{U}{V} = \frac{2}{3} U$$

If $\frac{n\lambda^3}{g} \gg 1$ – Weakly degenerate Fermi gas

$\frac{n\lambda^3}{g} \rightarrow \infty \rightarrow$ – Completely degenerate or Strongly degenerate

Strongly degenerate or Completely degenerate ideal fermi gas

$$f(E) = \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} + 1} = 1 \quad \text{for } \epsilon < \mu (= E_F)$$

$$= 0 \quad \text{for } \epsilon > \mu (= E_F)$$

Chemical potential at $T = 0$ is equal to Fermi energy

$$\mu = E_F, \quad \text{at } T = 0$$

Fermi level is that level for which the occupation no. $f(\epsilon_i)$ is $\frac{1}{2}$

$$N = \int_0^\infty f(E) g(E) dE$$

For strongly degenerate

$$N = \int_0^{E_F} 1 \times g(E) dE + \int_{E_F}^\infty 0 \times g(E) dE$$

$$= \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^{E_F} g(E) dE$$

$$N = \frac{4}{3} \frac{\pi V g_s}{h^3} (2m)^{3/2} E_F^{3/2} \Rightarrow E_F = \frac{h^2}{2m} \left(\frac{3N}{4\pi V g_s} \right)^{2/3} \rightarrow \text{strongly degenerate Fermi gas}$$

For electron or proton $g_s = 2$

$$E_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3} \quad \dots (1)$$



$$g_s = (2S+1) \text{ multiplicity due to spin} \quad E = \frac{p^2}{2m}$$

$$E_F = \frac{1}{2m} \left[h \left(\frac{3N}{4\pi V g_s} \right)^{\frac{1}{3}} \right]^2$$

$$= \frac{h}{2m} \left(\frac{6\pi^2 n}{g_s} \right)^{\frac{3}{2}} = 13.65 \times 10^{-19} n^{\frac{3}{2}} \text{ for electron}$$

$$p_F = \text{Fermi momentum} \rightarrow p_F = h \left(\frac{3N}{4\pi V g_s} \right)^{\frac{1}{3}} \quad E_F = k_B T_F$$

$T_F = \text{Fermi temp or degenerate temp for fermi gas}$

$$\text{So} \quad T_F = \frac{1}{k_B} \frac{h^2}{2m} \left(\frac{3N}{4\pi V g_s} \right)^{\frac{2}{3}}$$

Ground State Energy (E_0):

$$\begin{aligned} E_0 &= \int_0^\infty E f(E) g(E) dE = \int_0^{E_F} E f(E) g(E) dE + \int_{E_F}^\infty E \times f(E) g(E) dE \\ &= \int_0^{E_F} E \times 1 \times g(E) dE + \int_{E_F}^\infty E \times 0 \times g(E) dE \\ &= \int_0^{E_F} E \times g(E) dE \\ &= \frac{2\pi V g_s (2m)^{\frac{3}{2}}}{h^3} \int_0^{E_F} E^{\frac{3}{2}} dE \\ &= \frac{2\pi V g_s (2m)^{\frac{3}{2}}}{h^3} \times \frac{2}{5} E^{\frac{5}{2}} \Big|_0^{E_F} = \frac{4}{5} \frac{\pi V g_s (2m)^{\frac{3}{2}}}{h^2} E_F^{\frac{5}{2}} \end{aligned}$$

Average ground state energy

$$\frac{E_0}{N} = \frac{\frac{4}{5} \pi V g_s (2m)^{\frac{3}{2}} E_F^{\frac{5}{2}}}{\frac{4}{5} \frac{\pi V g_s (2m)^{\frac{3}{2}}}{h^3} E_F^{\frac{3}{2}}} = \frac{3}{5} E_F \quad \Rightarrow \quad \boxed{\frac{E_0}{N} = \frac{3}{5} E_F}$$

Ground state pressure of the system P

$$\begin{aligned} P_0 &= \frac{2}{3} \frac{E_0}{V} \\ &= \frac{2}{3} \times \frac{3}{5} \frac{N}{V} E_F = \frac{2}{5} n E_F \\ P_0 &= \frac{2}{5} n E_F \quad \Rightarrow \quad P_0 = \left(\frac{6\pi^2}{g_s} \right)^{\frac{2}{3}} \frac{h^2}{5m} n^{\frac{5}{3}} \\ P_0 &\propto n^{\frac{5}{3}} \end{aligned}$$

$P = 0$ for Bose gas

The zero point motion is clearly a quantum effect arising because of Pauli exclusion principle. According to which even at $T = 0$ the particles constituting the system can't accumulate into a single particle state (As can in B.E case) and are therefore spread over a requisite no. of lowest available energy state. As a result in Fermi system even at absolute zero quite exist.

The Fermi gas at finite temp but low (weakly degenerate) The no. of particle



$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^\infty \frac{e^{\mu/2}}{e^{\frac{\epsilon - \mu}{k_B T}} + 1} d\epsilon \quad \int_0^\infty \frac{Q(x) dx}{e^{x-\xi} + 1} = \int_0^\xi Q(x) dx + \frac{\pi^2}{6} \left(\frac{\partial Q}{\partial x} \right)_{x=\xi} + \frac{7\pi^4}{360} \left(\frac{d^3 Q}{dx^3} \right)_{x=\xi}$$

For low temp we can expand the integral by approximation upto 1st order I compare these two and take

$$\frac{\epsilon}{k_B T} = 1.$$

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^\mu \epsilon^{1/2} dt + \frac{\pi^2}{6} (k_B T)^2 \frac{1}{2} \mu^{-1/2}$$

$$= \frac{2\pi V g_s (2m)^{3/2}}{h^3} \frac{2}{3} \mu^{3/2} + \frac{\pi^2}{6} (k_B T)^2 \frac{1}{2} \mu^{-1/2}$$

$$= \frac{3N}{2E_f^{3/2}} \left[\frac{2\mu^{3/2}}{3} + \frac{\pi^2}{6} (k_B T)^2 \frac{1}{2} \mu^{-1/2} \right]$$

$$E_f^{3/2} = \frac{3}{2} \mu^{3/2} \left[\frac{2}{3} + \frac{\pi^2}{12} \left(\frac{k_B T}{\mu} \right)^2 \right] = \mu^{3/2} \left[1 + \frac{\pi^2}{18} \left(\frac{k_B T}{\mu} \right)^2 \right]$$

$$E_f(T) = E_f(0) \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_f(0)} \right)^2 + \dots \right]$$

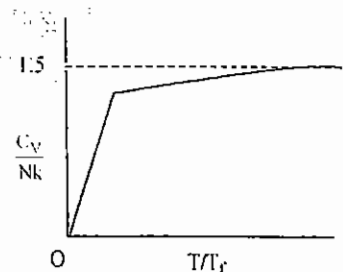
$$\frac{U}{N} = \frac{E}{N} = \frac{3}{5} E_f(0) \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_f(0)} \right)^2 \right]$$

$$P = \frac{2U}{3V} = \frac{2}{5} \frac{N}{V} E_f(0) \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_f(0)} \right)^2 \right]$$

$$\frac{C_V}{Nk} = \frac{\pi^2}{2} \frac{k_B T}{E_f(0)} \rightarrow \text{electronic specific heat in case of solid}$$

$$\frac{\Lambda}{N} = \mu - \frac{PV}{N}$$

$$= \frac{3}{5} E_f(0) \left[1 - \frac{5\pi^2}{12} \left(\frac{k_B T}{E_f(0)} \right)^2 + \dots \right]$$



$$\frac{S}{Nk_B} = \frac{\pi^2}{2} \frac{k_B T}{E_f(0)}$$

At $T \rightarrow 0$ $S \rightarrow 0$ in accordance with the third law of thermodynamics

For $T \ll T_f$ the specific heat varies as the first power of temperature moreover in magnitude it is considerable

smaller than the classical value $\frac{3}{2} Nk_B$.



Comparison of MB, BE and FD-statistics :

S.No.	Features	MB	BE	FD
1.	Particles	Distinguishable, the uncertainty relation and the Pauli's exclusion principle do not apply. Ex: gas particles at ordinary temp.	Indistinguishable, called bosons that do not obey Pauli's exclusion principle but obey uncertainty relation. Ex: photon and phonon gas.	Indistinguishable, called fermions that obey Pauli's exclusion principle and also the uncertainty relation Heisenberg. Ex: electron gas in metals.
2.	Particle spin	Spinless	0, 1, 2,	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
3.	Number of ways W in which N particle could be distributed in the g states.	$(g)^N$	$\frac{(N+g-1)!}{N!(g-1)!}$	$\frac{g!}{N!(g-N)!}$
4.	Wave function, ψ		Symmetric under interchange of the coordinates of any two bosons.	Antisymmetric on interchange of the coordinates of any two fermions
5.	Number of particles energy state	No upper limit	No upper limit per quantum state, as Pauli principle is not obeyed.	At best, only one per quantum state is allowed as Pauli principle is obeyed.
6.	Distribution function	$f(E) = e^{-E/kT}$	$f(E) = \frac{1}{e^{\alpha} e^{E/kT} - 1}$	$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$
7.	Total energy	$U = \frac{3}{2} NkT$	$\frac{3}{2} NkT \left(1 - \frac{1}{2^{5/2} e^{-\alpha}} \right)$	$\frac{3}{2} NkT \left(1 + \frac{1}{2^{5/2} e^{-\alpha}} \right)$
8.	Pressure	$p = \frac{NkT}{V}$	$\frac{NkT}{V} \left(1 - \frac{1}{2^{5/2} e^{-\alpha}} \right)$	$\frac{NkT}{V} \left(1 + \frac{1}{2^{5/2} e^{-\alpha}} \right)$



PREVIOUS YEARS SOLUTIONS OF TIFR

- Q. A gas of photons is enclosed in a container of fixed volume at an absolute temperature T . Noting that the photon is massless particle (i.e. its energy and momentum are related by $E = pc$), the number of photons in the container will vary as [TIFR 2014]

(a) T (b) T^2 (c) T^3 (d) T^4

Soln. The density of photon is $g(p)dp = Ap^2 dp$, A is a constant, where $p = E/c$.

$$\text{Therefore, } g(E)dE = A \frac{E^2}{c^3} dE$$

So the number of photons are

$$N = \int_0^\infty g(E) f(E) dE = A \int_0^\infty \frac{E^2}{c^3} \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1} dE, \text{ where } \mu = 0 \text{ (for photons).}$$

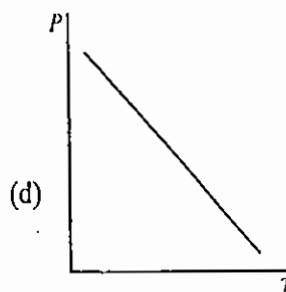
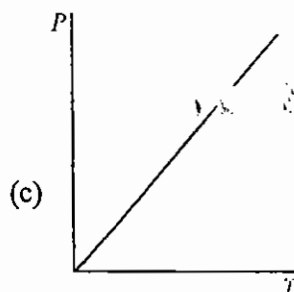
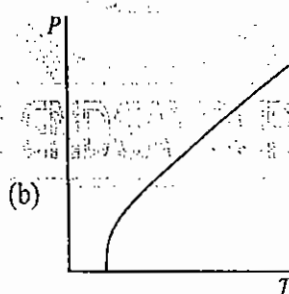
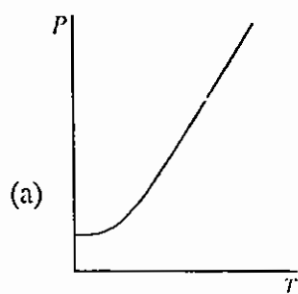
$$\text{Therefore, } N = \frac{A}{c^3} \int_0^\infty \frac{E^2}{\exp(E/k_B T) + 1} dE$$

Letting $\frac{E}{k_B T} = x$. Then,

$$N = \frac{A}{c^3} \int_0^\infty \frac{(k_B T x)^2}{e^x + 1} (k_B T) dx = k_B^3 \frac{A}{c^3} T^3 \int_0^\infty \frac{x^2}{e^x + 1} dx \Rightarrow N \propto T^3.$$

Correct option is (c)

- Q. Which of the following graphs qualitatively describes the pressure P of a gas of non-interacting fermions in thermal equilibrium at a constant volume as a function of temperature? [TIFR 2015]



Soln. The energy of fermions is $E = \int_0^\infty E f(E) g(E) dE$, where



$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \text{ and } g(E) = \frac{4\pi\sqrt{2}V}{h^3} m^{3/2} E^{1/2}.$$

$$\text{Therefore, } E = \frac{4\pi\sqrt{2}Vm^{3/2}}{h^3} \int_0^\infty \frac{E^{3/2}}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} dE \quad \dots (1)$$

$$\text{when } T = 0, \exp\left(\frac{E - E_F}{k_B T}\right) = 1, \text{ when } E < E_F$$

$$\text{Therefore, } E_{T=0} = \frac{4\pi\sqrt{2}Vm^{3/2}}{h^3} \int_0^{E_F} E^{3/2} dE = \frac{8\pi\sqrt{2}Vm^{3/2}}{h^3} \frac{E_F^{5/2}}{5}$$

$$\text{So, } P = \frac{2}{3} \frac{E}{V} = \frac{16\pi\sqrt{2}}{15} \frac{m^{3/2}}{h^3} E_F^{5/2}$$

Therefore, there is some pressure when $T = 0$.

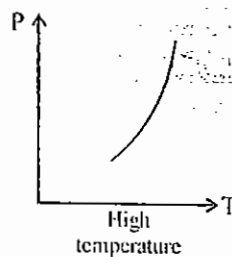
Now, letting $\frac{E - E_F}{k_B T} = x$. Then, equation (1) gives

$$E = \frac{4\pi\sqrt{2}Vm^{3/2}}{h^3} \int_0^\infty \frac{(k_B T x + E_F)^{3/2} k_B T dx}{e^x + 1}$$

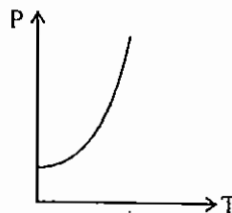
At high temperature, we have

$$E = \frac{4\pi\sqrt{2}Vm^{3/2}}{h^3} \int_0^\infty (k_B T)^{5/2} \frac{x^{3/2}}{e^x + 1} dx$$

Since $P = \frac{2}{3} \frac{E}{V}$, we have $P \propto T^{5/2}$ at high temperature. The corresponding graph is



So combining the values of P at $T = 0$ and high temperature, we have



Correct option is (a)



- Q. Bosonic excitations of ferromagnets have a dispersion relation $\epsilon = \gamma k^2$, where ϵ is the energy and k is the wavevector of the excitation. Assuming a system of such non-interacting bosonic excitation, at low temperature T , the specific heat C_V of a three dimensional ferromagnet will be proportional to [TIFR 2015]
- (a) T (b) $T^{3/2}$ (c) $T^{5/2}$ (d) T^3

Soln. The given relation is $\epsilon = \gamma k^2 = \frac{\gamma p^2}{\hbar^2}$

The density of state is $g(p)dp = Ap^2 dp$, where A is some constant.

Therefore, $g(\epsilon)d\epsilon = B\epsilon^{1/2}d\epsilon$, where B is some other constant.

Therefore, the average energy is

$$\langle \epsilon \rangle = \int_0^\infty \epsilon f(\epsilon) g(\epsilon) d\epsilon = \int_0^\infty \frac{B\epsilon^{3/2} d\epsilon}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1}$$

Letting $\frac{\epsilon - \mu}{k_B T} = x$. Then, $\langle \epsilon \rangle = B \int_0^\infty \frac{(k_B T x + \mu)^{3/2} (k_B T) dx}{e^x - 1}$

At low temperature, all the particles may be in the lowest energy level and hence $\mu \rightarrow 0$ at low temperature.

$$\therefore \langle \epsilon \rangle = B(k_B T)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx$$

$$\therefore \langle \epsilon \rangle \propto T^{5/2}$$

$$\therefore C_V = \left(\frac{d}{dT} \langle \epsilon \rangle \right) \propto T^{3/2}$$

Correct option is (b)

- Q. In two dimensions two metals A and B, have the number density of free electrons in the ratio $n_A : n_B = 1 : 2$. The ratio of their Fermi energies is [TIFR 2017]
- (a) 2 : 3 (b) 1 : 2 (c) 1 : 4 (d) 1 : 8

Soln. The Fermi energy is related to particle density as $E_F \propto n^{2/d}$, where d is the dimension.

Therefore, for two dimensions, we have $E_F \propto n$

$$\therefore \frac{(E_F)_A}{(E_F)_B} = \frac{n_A}{n_B} = \frac{1}{2}$$

Correct option is (b)

PREVIOUS YEARS SOLUTIONS OF JEST

- Q. An ideal gas of non-relativistic fermions in 3-dimensions is at 0K. When both the number density and mass of the particles are doubled, then the energy per particle is multiplied by a factor
- (a) $2^{1/2}$ (b) 1 (c) $2^{1/3}$ (d) $2^{-1/3}$

Soln. The number of fermions is

$$N = \int_0^\infty f(E) g(E) dE, \text{ where}$$



$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} = \begin{cases} 1 & , E > E_F \\ 0 & , E < E_F \end{cases} \text{ at } 0 \text{ K and } g(E) = \frac{4\pi\sqrt{2}V}{h^3} m^{3/2} E^{1/2}.$$

$$\therefore N = \frac{4\pi\sqrt{2}V}{h^3} m^{3/2} \int_0^{E_F} E_F^{1/2} dE = \frac{8\pi\sqrt{2}V}{3h^3} m^{3/2} E_F^{3/2}$$

$$\Rightarrow E_F = \frac{1}{m} \left(\frac{3h^3 n}{8\sqrt{2}\pi} \right)^{2/3} = \frac{h^2}{m} \left(\frac{3n}{8\pi\sqrt{2}} \right)^{2/3}$$

So if mass and number density gets doubled, the energy multiplied by the factor $2^{-1/3}$.

Correct option is (d)

- Q. For non-interacting Fermions in d -dimensions, the density of states $D(E)$ varies as $E^{(d/2-1)}$. The Fermi energy E_F of an N particle system in 3-, 2- and 1-dimensions will scale respectively as, [JEST 2015]

- (a) $N^2, N^{2/3}, N$ (b) $N, N^{2/3}, N^2$ (c) $N, N^2, N^{2/3}$ (d) $N^{2/3}, N, N^2$

Soln. The total number of fermions are $N = \int_0^\infty f(E)g(E)dE$, where

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} = \begin{cases} 1 & , E < E_F \\ 0 & , E > E_F \end{cases} \text{ at } 0 \text{ K}$$

and $g(E) = CE^{d/2-1}$, where C is a proportionality constant.

$$\text{Therefore, } N = C \int_0^{E_F} E^{d/2-1} dE = \frac{C}{d/2} E_F^{d/2}.$$

$$\Rightarrow E_F \propto N^{2/d}$$

$$\Rightarrow E_F \propto \begin{cases} N^{2/3} & \text{when } d=3 \\ N & \text{when } d=2 \\ N^2 & \text{when } d=1 \end{cases}$$

Correct option is (d)

- Q. Consider N non-interacting electrons ($N \sim N_A$) in a box of sides L_x, L_y, L_z . Assume that the dispersion relation is $\varepsilon(k) = Ck^4$, where C is a constant, the ratio of the ground state energy per particle to the Fermi energy is: [JEST 2016]

- (a) $\frac{3}{7}$ (b) $\frac{7}{3}$ (c) $\frac{3}{5}$ (d) $\frac{5}{7}$

Soln. The ground state per particle is

$$\frac{E_0}{N} = \frac{\int_0^\infty E f(E) g(E) dE}{\int_0^\infty f(E) g(E) dE}$$



At $T = 0\text{K}$, $f(E) = 1$ and $E_{\text{max}} = E_F$

$$\therefore \frac{E_0}{N} = \frac{\int_0^{E_F} E g(E) dE}{\int_0^{E_F} g(E) dE}$$

where $g(E) dE = g(p) dp$

$$= \frac{4\pi V}{h^2} p^2 dp = \frac{4\pi V}{h^2} \hbar^3 k^2 dk = \frac{4\pi V}{h^2} \hbar^3 \frac{\epsilon^{1/2}}{4C^{3/4}} \epsilon^{-3/4} d\epsilon$$

$$\therefore g(E) \propto \epsilon^{-1/4}$$

$$\therefore \frac{E_0}{N} = \left(\frac{E_F^{7/4}}{7/4} \right) \left(\frac{3/4}{E_F^{3/4}} \right) = \frac{3}{7} E_F$$

$$\therefore \frac{E_0/N}{E_F} = \frac{3}{7}$$

Correct option is (a)

- Q. A cylindrical at temperature $T = 0$ is separated into two compartments A and B by a free sliding piston. Compartments A and B are filled by Fermi gases made of spin $1/2$ and $3/2$ particles respectively, If particles in both the compartments have same mass, the ratio of equilibrium density of the gas in compartment A to that of gas in compartment B is [JEST 2017]

- (a) 1 (b) $\frac{1}{3^{2/5}}$ (c) $\frac{1}{2^{2/5}}$ (d) $\frac{1}{2^{2/3}}$

Soln. The pressure is given by $P = \frac{2}{5} n \epsilon_F$

$$\text{where, } \epsilon_F = \left(\frac{6\pi^2 n}{g_s} \right)^{2/3} \frac{\hbar^2}{2m}$$

$$\therefore P = \frac{2}{5} n \left(\frac{6\pi^2 n}{g_s} \right)^{3/2} \frac{\hbar^2}{2m}$$

At equilibrium, we have $P_A = P_B$

$$\Rightarrow n_A \left(\frac{n_A}{g_{sA}} \right)^{3/2} = n_B \left(\frac{n_B}{g_{sB}} \right)^{3/2}$$

$$\text{where, } g_{sA} = 2 \times \frac{1}{2} + 1 = 2 \text{ and } g_{sB} = 2 \times \frac{3}{2} + 1 = 4$$

$$\therefore \frac{n_A}{n_B} = \frac{1}{2^{2/5}}$$

Correct option is (c)

Chapter 8

Physics of Black-Body Radiation & Phase Transition

Prevost's theory of heat exchange

According to this theory all bodies radiate thermal radiation at all temperature. The amount of thermal radiation radiated per unit time depends on the nature of emitting surface, its area and temperature. The rate is faster at high temperature. Beside a body also absorbs a part of the thermal radiation emitted by the surrounding bodies when the radiation falls on it at a rate depending on the surface and temperature of the surrounding bodies. If a body radiates more than what it absorbs its temperature falls. If a body radiates less than what it absorbs its temperature rises.

Note :

1. When the temp of a body is equal to the temperature of its surroundings it radiates at the same rate as it absorbs.
2. The thermal equilibrium between any body and its surrounding is dynamical equilibrium.
3. The radiation inside an enclosure is homogeneous and isotropic.
4. The radiation inside a uniform temperature enclosure depends only on the temperature and not on the nature of the walls of the enclosure or on the bodies present inside it.
5. The radiation inside an enclosure is identical with the radiation emitted by a perfectly black body at same temperature.

Black body radiation : A body that absorbs all the radiation of any wavelength falling on it, is called black body. Such body emits radiation at the fastest rate. The radiation emitted by blackbody is called black body radiation.

Kirchoff's law : For a given wavelength the ratio of emissive power to absorptive power is same for all bodies at a given temperature and is equal to the emissive power of a black body or perfectly black body at that temperature.

$$\frac{e_{\lambda}}{a_{\lambda}} = E_{\lambda}$$

Stefan's law : According to this law energy radiated per unit time per unit area for any body is directly proportional to the fourth power of absolute temperature.

$$E \propto T^4$$

$$E = \sigma T^4 \quad \rightarrow \text{For perfectly black body}$$

$$E = e \sigma T^4 \quad \rightarrow \text{For any body}$$

$$\sigma = \text{Stefan's constant} = 5.67 \times 10^{-8} \text{ watt/m}^2\text{K}^4$$



The net rate of flow of radiation per unit area $= \frac{1}{4} \frac{U}{V} C$

Stefan - Boltzmann law : Energy radiated per unit time per unit area is given by

$$E = e \sigma (T^4 - T_0^4)$$

where $T \rightarrow$ absolute temperature of surface that emits radiation

$T_0 \rightarrow$ absolute temperature of external atmosphere or surrounding

Let T be the temperature of any body that is slightly greater than temperature of surrounding T_0 such that

$$T - T_0 = t \Rightarrow T = t + T_0$$

$$E = e \sigma [(T_0 + t)^4 - T_0^4]$$

$$= e \sigma T_0^4 \left[\left(1 + \frac{t}{T_0} \right)^4 - 1 \right] = 4 \sigma T_0^3 t = 4 \sigma T_0^3 (T - T_0)$$

$$E \propto T - T_0 \rightarrow \text{Newton's law of cooling}$$

It is limited to small temperature difference:

The most important application of B.E statistics is to investigate the equilibrium properties of black body radiation we consider a radiation cavity of volume V and temperature T

The system can be looked upon from two practically identical but conceptually different point of view.

(1) As an assembly of harmonic oscillator with quantised energies

$$E_s = \left(n_s + \frac{1}{2} \right) \hbar \omega_s \quad n_s = 0, 1, 2, \dots$$

Where $\omega_s \rightarrow$ frequency of vibration

(2) As a gas of identical & indistinguishable quanta (photon)

The energy of photon corresponding to frequency ω_s of the radiation mode being $\hbar \omega_s$.

The distribution of photon in various quantum state of energy is given by

$$\langle n_s \rangle = f(\epsilon_s) = \frac{1}{\exp[\epsilon_s / k_B T] - 1} \quad (\mu = 0 \text{ for photon gas})$$

The no. of vibrational modes of EM wave in frequency range

ν and $\nu + d\nu$ is given by

$$= 2 \times \frac{4\nu\pi}{h^3} p^2 dp$$

$$= \frac{8\pi V \nu^2 d\nu}{c^3}$$

$$p = \frac{h\nu}{c}$$

Two factor is due to transverse nature i.e two direction tr to the direction of propagation

Average no. of photons between frequency range ν and $\nu + d\nu$

$$N(\nu) d\nu = \frac{2 \times V 4\pi p^2 dp}{h^3 \left(e^{\frac{h\nu}{k_B T}} - 1 \right)} = \frac{8\pi V \nu^2 d\nu}{c^3 \left(e^{\frac{h\nu}{k_B T}} - 1 \right)}$$

Total no. of photons in cavity of volume V



$$\frac{8\pi V}{c^3} \int \frac{\nu^2 d\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

$$\text{Let } \frac{h\nu}{k_B T} = x \Rightarrow d\nu = \frac{k_B T}{h} dx$$

$$= \frac{8\pi V}{c^3} \int_0^\infty \frac{\left(\frac{k_B T}{h}\right)^3 x^2 dx}{e^x - 1} \Rightarrow N \propto T^3$$

The energy of photon in the range is $h\nu$ (radiant frequency in the range ν to $\nu + d\nu$)

$$U(\nu)d\nu = \frac{V 8\pi \nu^3}{c^3} \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} d\nu \quad \dots (1)$$

Planck's formula for spectral energy distribution
per unit Volume of black body radiation

Spectral energy density in the range λ to $\lambda + d\lambda$

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

$$c = \nu\lambda \Rightarrow \nu = \frac{c}{\lambda}$$

$$d\nu = -\frac{c}{\lambda^2} d\lambda$$

(i) On longer wavelength (Smaller frequency side)

$$\frac{hc}{\lambda} \ll k_B T \quad \text{or } h\nu \ll k_B T$$

$$u(\lambda)d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$$

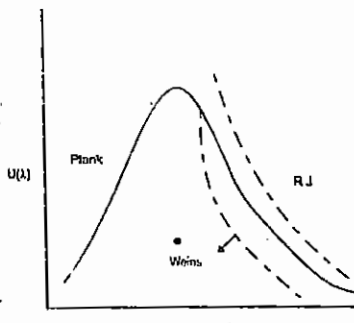
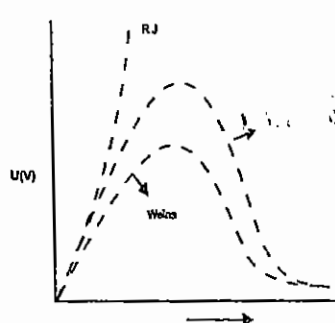
Rayleigh Jean's law

(ii) on short wavelength (Longer frequency side)

$$\frac{hc}{\lambda} \gg k_B T \quad h\nu \gg k_B T$$

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} e^{-\frac{hc}{\lambda k_B T}} d\lambda$$

Wein's law



Deduction of Stefan's law from Planck's law :

At equilibrium total energy of the black body radiation inside an enclosure of volume V (Black body radiation) at temperature T is given by



$$U(\nu) d\nu = \frac{8\pi V}{c^3} \frac{h\nu^3}{e^{h\nu/k_B T} - 1}$$

Total energy

$$U(T) = \int_0^\infty U(\nu) d\nu = \int_0^\infty \frac{8\pi V h \nu^3}{c^3 (e^{h\nu/k_B T} - 1)} d\nu = \frac{8\pi V h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}$$

$$\frac{h\nu}{k_B T} = x \quad \Rightarrow \quad d\nu = \frac{k_B T}{h} dx$$

Put

$$U(T) = \frac{8\pi V}{(hc)^3} (k_B T)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$

$$= \frac{8\pi V}{(hc)^3} (k_B T)^4 \times \frac{\pi^4}{15} = \frac{8}{15} \pi^5 \frac{V (k_B T)^4}{(hc)^3}$$

$$\frac{U(T)}{V} = \frac{8}{15} \pi^5 \frac{(k_B T)^4}{(hc)^3}$$

The net rate of flow of radiation per unit area

$$E = \frac{1}{4} \frac{U}{V} C = \frac{8}{10} \pi^5 \frac{k_B^4 T^4}{h^3 c^2}$$

$$= \sigma T^4 \quad \text{where } \sigma = \frac{8}{60} \pi^5 \frac{k_B^4}{h^3 c^2}$$

By substituting the usual value $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4$

Q. Use Planck's formula to obtain expression for (a) Stefan's constant and (b) Wein's constant in terms of Planck's constant and Boltzmann's constant.

Soln. Using Planck's formula the total radiant energy in unit volume of an isothermal enclosure is given by

$$U = \int_0^\infty E_\lambda d\lambda = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5 \left(e^{\frac{hc}{\lambda k_B T}} - 1 \right)} \quad \dots (i)$$

But the total radiant energy in unit volume of an isothermal enclosure is also given by

$$U = AT^4 \quad \dots (ii)$$

where $A = \text{constant}$ $T = \text{absolute temperature of the enclosure}$ comparing eqn (i) and (ii) we have

$$AT^4 = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5 \left(e^{\frac{hc}{\lambda k_B T}} - 1 \right)}$$

Putting $x = \frac{hc}{\lambda k_B T}$ or $\lambda = \frac{hc}{x k_B T} \Rightarrow d\lambda = \frac{-hc}{x^2 k_B T} dx$

we have $AT^4 = 8\pi hc \int_0^\infty \frac{\frac{hc}{x^2 k_B T}}{\left(\frac{hc}{x k_B T} \right)^5 (e^x - 1)} dx$



$$= 8\pi hc \times \frac{hc}{k_B T} \times \left(\frac{k_B T}{hc}\right)^5 \int_0^\infty \frac{x^5}{x^2(e^x - 1)} dx = \frac{8\pi k_B^4 T^4}{h^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

$$\left[\int_0^\infty \frac{x^n dx}{e^x - 1} = \frac{\pi^{n+1}}{1.35 \dots (2n-1)} \right]$$

$$AT^4 = \frac{8\pi k_B^4 T^4}{h^3 c^3} \times \frac{\pi^4}{1.35} = \frac{8\pi^5 k_B^4 T^4}{15 h^3 c^3} \Rightarrow A = \frac{8\pi^5 k_B^4}{15 h^3 c^3}$$

Since Stefan's constant (a) is given by

$$a = \frac{Ac}{4} = \frac{8\pi^5 k_B^4}{15 \times 4 h^3 c^3} \times c = \frac{2}{15} \frac{\pi^5 k_B^4}{h^3 c^2} \rightarrow \text{Stefan's constant}$$

Weins constant : According to Wein's law Wein's constant is given by $b = \lambda_m T$

where λ_m is the wavelength for which the emitted energy is maximum and the expression for it

$$\lambda_m = \frac{hc}{9.965 k_B T}, \quad \lambda_m T = \frac{hc}{9.965 k_B}$$

The weins constant $b (= \lambda_m T)$ is given by

$$b = \frac{hc}{9.965 k_B}$$

Solar Constant: In the absence of atmosphere the energy of sun rays incident per unit area per minute perpendicular to the surface at average distance of earth from sun is called solar constant.

Let r is the radius of sun, R is the average distance of earth from sun. Consider sun as black body.

$$S = \frac{4\pi r^2 \times \sigma T^4}{4\pi R^2} \text{ or } T^4 = \frac{S R^2}{\sigma r^2} \text{ where } \sigma \text{ is Stefan's constant.}$$

Q. Consider a radiation cavity of volume V at temperature T . The density of states at energy E of the quantized radiation (photons) is:

(a) $\frac{8\pi V}{h^3 c^3} E^2$ (b) $\frac{8\pi V}{h^3 c^3} E^{3/2}$ (c) $\frac{8\pi V}{h^3 c^3} E$ (d) $\frac{8\pi V}{h^3 c^3} E^{3/4}$

Soln. It is well known that the nodes are formed at the end points of the string due to stationary vibrations and only certain discrete frequencies of vibrations are allowed. If l is the length of the string, the allowed wavelength are given by

$$\lambda = \frac{2l}{n} \quad \dots(i)$$

$$n = 1, 2, 3, 4, \dots, \infty$$

$$\text{The corresponding allowed frequencies are } \nu = \frac{c}{\lambda} = \frac{nc}{2l}$$

$$n = 1, 2, 3, 4, \dots, \infty \quad \text{where, } c \text{ is the speed of the waves.}$$

In this case, the wave are confined to a three-dimensional space. Let each side of the cube be a . If we take the three intersecting edges of the cube as X, Y and Z-axis of a Cartesian coordinate system and $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ as direction cosines of the direction of propagation of a particular wave, then the projections of the edges of the cube on the direction of propagation of the wave are $a \cos \alpha$, $a \cos \beta$ and $a \cos \gamma$.



respectively. In this case, the allowed wavelengths have to satisfy three conditions of the kind of equation (i), in which l is replaced by $a \cos \alpha$, $a \cos \beta$ and $a \cos \gamma$ respectively. Thus, an allowed wavelength λ must satisfy

$$\lambda = \frac{2a \cos \alpha}{n_1}, \quad \lambda = \frac{2a \cos \beta}{n_2} \quad \text{and} \quad \lambda = \frac{2a \cos \gamma}{n_3}$$

where, n_1, n_2 and n_3 are positive integers.

Using, trigonometric condition of direction cosines,

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \quad \dots(ii)$$

Substituting values of $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ in equation (ii), we have

$$\frac{n_1^2 \lambda^2}{4a^2} + \frac{n_2^2 \lambda^2}{4a^2} + \frac{n_3^2 \lambda^2}{4a^2} = 1 \quad \text{or} \quad n_1^2 + n_2^2 + n_3^2 = \frac{4a^2}{\lambda^2} = \left(\frac{2a}{\lambda}\right)^2 \quad \dots(iii)$$

$$\text{As } \lambda = \frac{c}{\nu}, \text{ we have } n_1^2 + n_2^2 + n_3^2 = \left(\frac{2a\nu}{c}\right)^2 \quad \dots(iv)$$

The number of modes of vibrations within the frequency interval ν and $\nu + d\nu$ can be found with the help of equation (iv).

For simplicity, let us first count the modes of vibration in an analogous two-dimensional problem. The two-dimensional equation will be

$$n_1^2 + n_2^2 = \left(\frac{2a\nu}{c}\right)^2 \quad \dots(v)$$

This represents a circle of radius $\left(\frac{2a\nu}{c}\right)$.

Thus, the number of modes of vibration within frequency interval ν and $\nu + d\nu$ is equal to the area in the

positive quadrant lying between two circles of radii $\frac{2a\nu}{c}$ and $\frac{2a(\nu + d\nu)}{c}$.

$$\text{Area} = \frac{1}{4} \pi \left[\left\{ \frac{2a(\nu + d\nu)}{c} \right\}^2 - \left(\frac{2a\nu}{c} \right)^2 \right] = \frac{\pi}{4} \times \frac{8a^2 \nu d\nu}{c^2} = \frac{2\pi a^2 \nu}{c^2} d\nu$$

The number of modes of vibration within frequency range ν and $\nu + d\nu$ is now equal to the volume of the

constant $(1/8)^{\text{th}}$ of the spherical shells with radii $\frac{2a\nu}{c}$ and $\frac{2a(\nu + d\nu)}{c}$ i.e.,

$$= \frac{1}{8} \left[\frac{4}{3} \pi \left(\frac{2a\nu}{c} \right)^3 - \frac{4}{3} \pi \left(\frac{2a(\nu + d\nu)}{c} \right)^3 \right]$$

$$= \frac{1}{8} \times \frac{4}{3} \pi \times \frac{8a^3}{c^3} \left[\nu^3 - (\nu + d\nu)^3 + 3\nu^2 d\nu \right]$$

$$= \frac{4\pi a^3 \nu^2}{c^3} d\nu$$

But $a^3 = V = \text{volume of the cube}$



Therefore, the modes of vibration inside cubical enclosure with frequency range ν and $\nu + d\nu$ will be

$$= \frac{4\pi V \nu^2 d\nu}{c^3}$$

\therefore Number of modes of vibration per unit volume with frequency range ν and $\nu + d\nu$ will be

$$= \frac{4\pi \nu^2 d\nu}{c^3}$$

Since, the black body radiation travel with velocity of light c and are transversed in character and hence, modes of vibrations are double as that for longitudinal waves.

Therefore, for black body radiation or electromagnetic waves, the number of modes of vibration per unit volume within frequency range ν and $\nu + d\nu$ will be

$$= 2 \times \frac{4\pi \nu^2 d\nu}{c^3} = \frac{8\pi \nu^2 d\nu}{c^3} \quad \dots(vi)$$

$\therefore \nu = E/h$, hence, it is clear from equation (vi) the number of modes of vibration or density of states is

$$8\pi V E^2 / h^2 c^3.$$

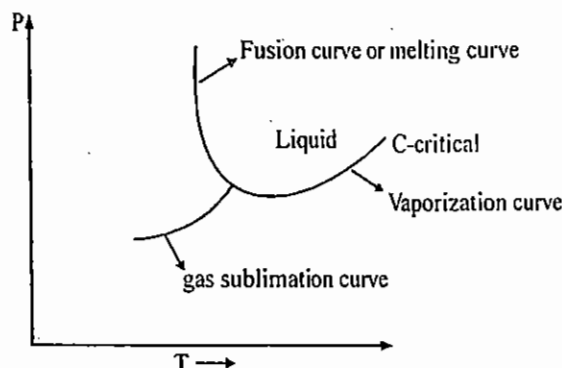
Hence correct option is (a).



Phase Transition

Phase transition : We consider a system whose phases are in equilibrium. In slight variation of external condⁿ (T,P) results a certain amount of the substance passing from one phase to another and this phenomena is called phase transition

Phase diagram :



- Triple point :** The point (unique temperature and pressure) at which all three phases can co-exist in equilibrium with each other is called triple point.

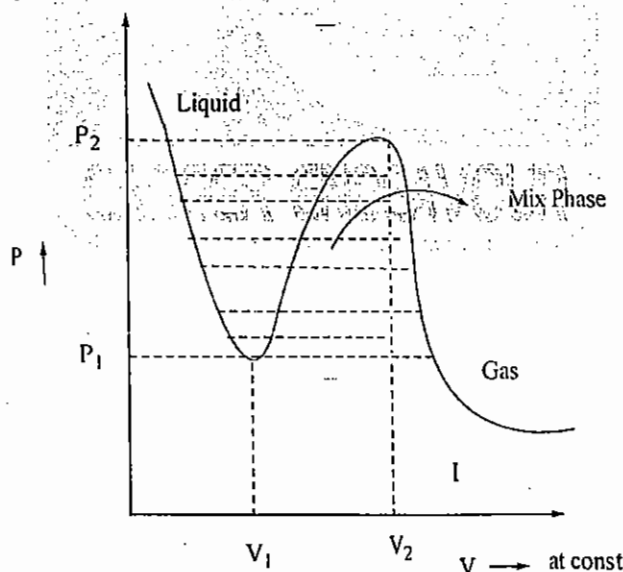
or

The point at which three curves intersect is known as triple point.

Critical point :

The point at which liquid vapour equilibrium lying ends. Above the critical point there is no further phase transition. Since there exist only one phase (gas or liquid)

In the shaded region mixture of two phases can co-exist along the horizontal line. At a given temperature T for $P < P_1$ there must be unique value of V for each value of P . Then there exist a well defined single phase.



$\frac{\partial P}{\partial V}$ for region I is small. So isothermal compressibility $-\frac{1}{V} \frac{\partial V}{\partial P}$ is large as in case of gaseous phase

At a given temperature for $P > P_2$ there are also unique value of V for each value of P . For this part $\frac{\partial P}{\partial V}$ is large,

So compressibility is small as in the case of liquid phase.

In the region $P_1 < P < P_2$ there is no unique value of V for each value of P . In this region there is a mixture of two phases that co-exist along the horizontal line.



First order phase transition :

We shall consider the condⁿ of equilibrium of two phases. Gibb's free energy is a function of (T, P, N) i.e $G = G(T, P, N)$

At constant T and P $G = N g(T, P)$ so $\mu = \frac{G}{N} = g(T, P)$

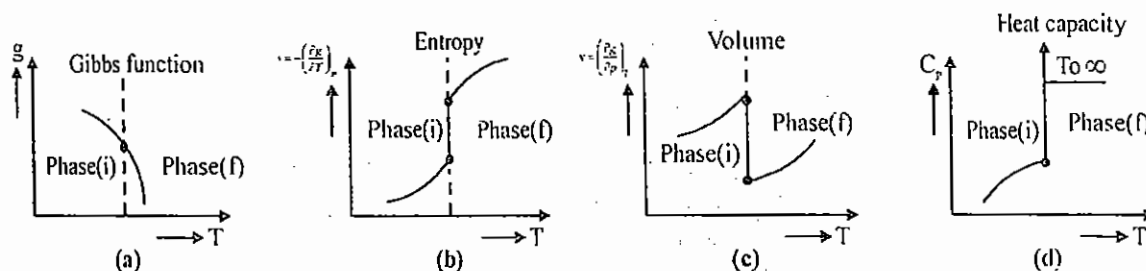
$$G = A + PV = U - TS + PV$$

$$Nd\mu + \mu dN = TdS - PdV - TdS - SdT + PdV + VdP + \mu dN$$

$$Nd\mu = -SdT + VdP \quad \Rightarrow \quad d\mu = \frac{-S}{N}dT + \frac{V}{N}dP$$

$$S = -\left(\frac{\partial \mu}{\partial T}\right)_P N = -\left(\frac{\partial G}{\partial T}\right)_P \quad \Rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$



First order phase transition can be characterised by either of following statement

(i) First order derivative of free energy change discontinuously or first order derivative of free energy are discontinuous at transition point.

Example: Entropy, volume, magnetisation, density are discontinuous.

The density changes discontinuously at transition point.

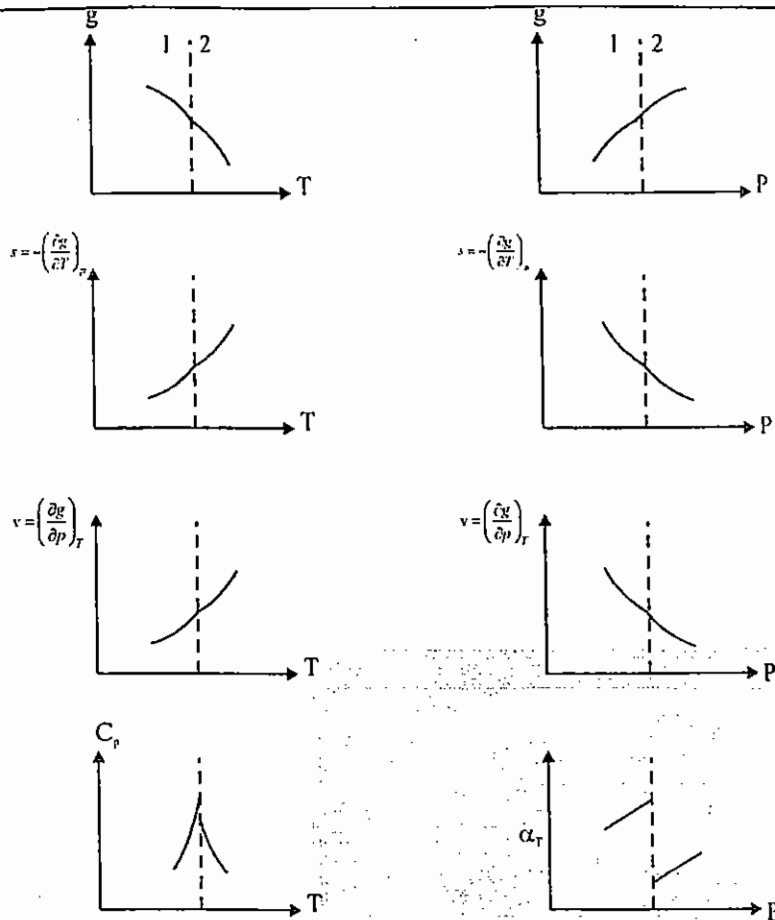
Example:

1. Vapour liquid transition away from the critical point (Along vapourisation curve)
- (ii) Conversion of water into water vapour.

Second order phase transition : If the 1st order derivative of free energy are continuous and 2nd order are discontinuous at transition point then the phase transition is called 2nd order phase transition or continuous phase transition.

The 2nd order phase transition is continuous in the sense that the state of the body changes continuously but discontinuous in the sense that the symmetry of the body changes discontinuously (specific heat, susceptibility

$$\chi = \frac{M}{H} = \frac{\partial M}{\partial H} \quad \text{compressibility} \quad \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right) \text{ are discontinuous.}$$



Second-order phase transitions

- Ex →
1. Transition of He-I to He-II for common isotope ${}^4\text{He}$
 2. Transition from non-ferro magnetic to Ferromagnetic
 3. Ferromagnetic to paramagnetic
 4. Transition from super conducting to conducting state & vice-versa
 5. Phase transition of liquid gas at critical points.

- Q. The vapour pressure P (in mm of Hg) of a solid at temperature T expressed by $\ln P = 23 - \frac{3863}{T}$ and that of its liquid phase by $\ln P = 19 - \frac{3063}{T}$. For triple point of the material temp is
- (a) 200 (b) 195 (c) 300 (d) 260

Soln. For triple point

$$23 - \frac{3863}{T} = 19 - \frac{3063}{T}$$

$$\frac{3863}{T} - \frac{3063}{T} = 23 - 19$$

$$800 = 4T \Rightarrow T = 200$$

- Q. Show that with the increase in pressure, boiling point of liquid increases and the melting point of substances which contract on melting decreases.

Soln. In case of boiling V_2 represents the specific volume of the vapour and V_1 that of the liquid phase of the substance

For all substances the specific volume in vapour phase is always larger than that in the liquid phase

Thus if the liquid phase is changed into vapour phase $V_2 - V_1$ is always +ve it follows from the Clapeyron's equation.



$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

will be +ve since L & T are essentially +ve quantities. Hence in case of the boiling point of a liquid an increase in pressure ($dP > 0$) will give a +ve value of dT .

It means the boiling points is raised by an increase in pressure. It has been found true for all liquids.

Change in melting point : In case of melting V_1 & V_2 represents the specific volumes of the substances in the solid & liquid phase respectively.

Now with the increase in pressure dT will be +ve if $V_2 - V_1$ is +ve (if $V_2 > V_1$) and dT will be -ve if $V_2 - V_1$ is -ve (if $V_2 < V_1$).

Thus the substances which expands on melting $\frac{dP}{dT}$ is +ve i.e. the melting point of substance which expands on melting increases with increase of pressure.

On the other hand if $V_2 < V_1$ i.e. for substances which contracts on melting $\frac{dP}{dT}$ is -ve & therefore melting point of substances which contracts on melting decreases with increase of pressure.

PREVIOUS YEARS SOLUTIONS OF TIFR

- Q.** In a cold country, in winter, a lake was freezing slowly. It was observed that it took 2 hours to form a layer of ice 2 cm thick on the water surface. Assuming a constant thermal conductivity throughout the layer, the thickness of ice would get doubled after [TIFR 2015]

(a) 2 more hours (b) 4 more hours (c) 6 more hours (d) 8 more hours

Soln. The rate of flow of heat in the water of lake will be

$$\frac{\Delta Q}{\Delta t} = \frac{KA\Delta T}{\ell}$$

where to freeze the water of lake into ice, we have $\Delta Q = mL_f$

$$\therefore \frac{mL_f}{\Delta t} = \frac{KA\Delta T}{\ell}$$

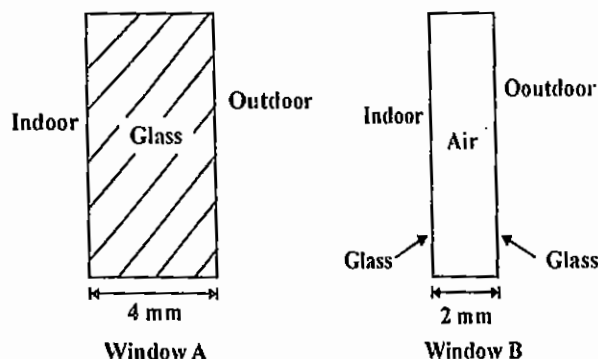
where $m = \rho V = \rho A\ell$

$$\therefore \Delta t \propto \ell^2 \quad \therefore \frac{\Delta t_2}{\Delta t_1} = \left(\frac{\ell_2}{\ell_1}\right)^2 \Rightarrow \Delta t_2 = \left(\frac{4}{2}\right)^2 \times 2 = 8 \text{ hours.}$$

\therefore Required time = 8 - 2 = 6 hours.

Correct option is (c)

- Q.** A manufacturer is able to offer two models of heat-conserving windows, as described below





Window A is a simple pane of glass, 4 mm thick. Window B, on the other hand, consists of two extremely thin panes of glass, separated by an air gap of 2 mm, as shown in the figure below above. If the thermal conductivity of glass is known to be $0.8 \text{ Wm}^{-1}\text{K}^{-1}$ and that of air is $0.025 \text{ Wm}^{-1}\text{K}^{-1}$, then the ratio of heat flow Q_A through window A to the heat flow Q_B through Window B is given by [TIFR 2014]

$$\frac{Q_A}{Q_B} =$$

(a) $\frac{1}{16}$

(b) $\frac{1}{4}$

(c) 4

(d) 16

Soln. The rate of flow of heat is

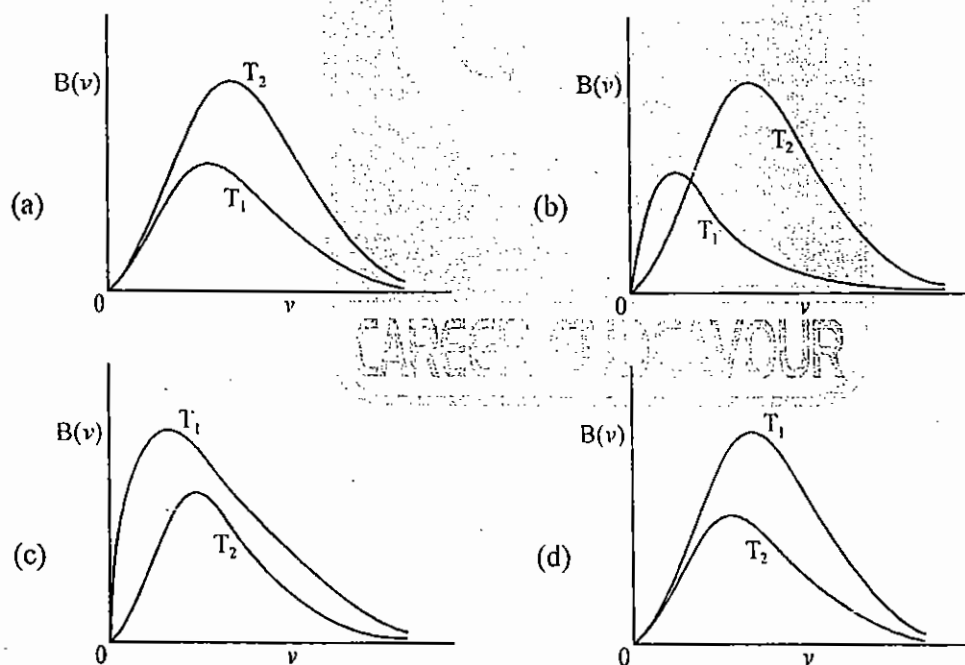
$$\frac{Q_A}{\Delta t} = \frac{K_A \Delta T}{\ell}$$

$$\therefore \frac{Q_A}{Q_B} = \frac{K_A \ell_B}{K_B \ell_A}, \text{ where the area of both windows and temperature difference is same.}$$

$$\therefore \frac{Q_A}{Q_B} = \frac{0.8}{0.025} \times \frac{2}{4} = 16.$$

Correct option is (d)

Q. Two blackbodies radiate energy at temperature T_1 and T_2 ($T_1 > T_2$). The energy emitted per unit time per unit solid angle per unit surface area of a blackbody in the frequency range ν to $\nu + d\nu$ is given by $B(\nu)d\nu$. Which one of the following graphs has the correct form? [TIFR 2015]



Soln. The Wien's displacement law gives $\lambda_m T = \text{constant}$.

$$\Rightarrow \frac{T}{\nu_m} = \text{constant where } \lambda_m \nu_m = c, T \text{ is the temperature of the body and } \nu_m \text{ is the frequency where}$$

$B(\nu)$ is maximum.

$\therefore T_1 > T_2$, we have

$$(\nu_m)_1 > (\nu_m)_2$$

Correct option is (d)



- Q. A binary star is observed to consist of a blue star B (peak wavelength 400 nm) and a red star R (peak wavelength 800 nm) orbiting each other. As observed from the Earth, B and R appear equally bright. Assuming that the stars radiate as perfect blackbodies, it follows that the ratio of volumes V_B/V_R of the two stars is [TIFR 2013]

- (a) $\frac{1}{64}$ (b) 64 (c) 16 (d) $\frac{1}{16}$

Soln. Since star B and star R appear to be equally bright, their power must appear to same from the Earth. So, $P_A = P_B$.

$$\Rightarrow S_R T_R^4 = S_B T_B^4, \text{ where } S_i \text{ represents the surface of star } i \text{ of radius } r_i \text{ and temperature } T_i.$$

$$\Rightarrow r_R^2 T_R^4 = r_B^2 T_B^4$$

$$\therefore \frac{r_B}{r_R} = \left(\frac{T_R}{T_B} \right)^2 = \left(\frac{\lambda_B}{\lambda_R} \right)^2$$

where we have used the Wien's displacement law, i.e., $\lambda T = \text{constant}$.

$$\therefore \frac{r_B}{r_R} = \left(\frac{400}{800} \right)^2 = \frac{1}{4}$$

$$\therefore \frac{V_B}{V_R} = \left(\frac{r_B}{r_R} \right)^3 = \frac{1}{64}$$

Correct option is (a)

- Q. A closed, thermally-insulated box contains one mole of an ideal monatomic gas G in thermodynamic equilibrium with blackbody radiation B. The total internal energy of the system is $U = U_G + U_B$ where U_G and $U_B (\propto T^4)$ are the energies of the ideal gas and the radiation respectively. If $U_G = U_B$ at a certain temperature T_0 K, then the energy required to raise the temperature from T_0 K to $(T_0 + 1)$ K, in terms of the gas constant R, is

- (a) 7.5 R (b) 6 R (c) 1.5 R (d) 0.33 R [TIFR 2011]

Soln. For an ideal monoatomic gas, we have

$$U_G = \frac{3}{2} nRT = \frac{3}{2} RT \quad (\text{For 1 mole})$$

and for a blackbody, we have

$$U_B = aT^4 \quad (\text{Given})$$

where 'a' is some proportionality constant.

Given : At $T = T_0$, we have $U_G = U_B$

$$\Rightarrow \frac{3}{2} RT_0 = aT_0^4 \Rightarrow T_0^3 = \frac{3R}{2a}$$

Therefore, the required energy is

$$\Delta U = \Delta U_G + \Delta U_B$$

$$= \frac{3}{2} R[(T_0 + 1) - T_0] + a[(T_0 + 1)^4 - T_0^4] = \frac{3}{2} R + aT_0^4 \left[\left(1 + \frac{1}{T_0} \right)^4 - 1 \right]$$

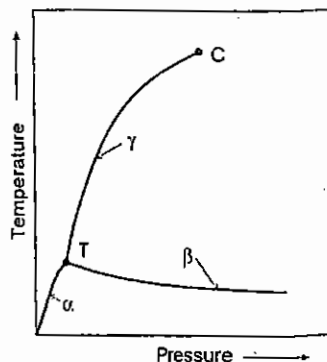


Using $(1+x) \approx 1+nx$, when $x \ll 1$, we have

$$\Delta U = \frac{3}{2}R + 4aT_0^3 = \frac{3}{2}R + 4a\left(\frac{3R}{2a}\right) = 7.5R.$$

Correct option is (a)

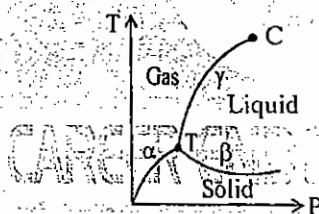
- Q. The phase diagram of a pure substance is given in the figure below, where 'T' denotes the triple point and 'C' denotes the critical point. [TIFR 2011]



The phase transitions occurring along the lines marked α , β and γ are

- (a) α = melting; β = condensation; γ = sublimation
- (b) α = sublimation; β = vaporisation; γ = melting
- (c) α = melting; β = vaporisation; γ = condensation
- (d) α = sublimation; β = melting; γ = vaporisation

Soln. Since α is a line between gas and solid phase, α represents sublimation. Similarly β represents melting and γ represents vaporisation.



Correct option is (d)

- Q. A many-body system undergoes a phase transition between two phases A and B at a temperature T_c . The temperature-dependent specific heat at constant volume C_V of the two phases are given by $C_V^{(A)} = aT^3 + bT$ and $C_V^{(B)} = cT^3$. Assuming negligible volume change of the system, and no latent heat generated in the phase transition, T_c is [TIFR 2018]

- (a) $\sqrt{\frac{2b}{c}}$
- (b) $\sqrt{\frac{b}{c-a}}$
- (c) $\sqrt{\frac{3b}{c-a}}$
- (d) $\sqrt{\frac{4b}{c-a}}$

Soln. The change in entropy of phase A is

$$\Delta S_A = \int_0^{T_c} C_V^{(A)} \frac{dT}{T},$$

where $S_A(T=0)$ is zero using third law of thermodynamics.

$$\therefore S_A(T) = \frac{aT^3}{3} + bT$$



Similarly, $S_B(T) = \frac{cT^3}{3}$

Since, there is no involvement of latent heat, the phase transition must be of second order and hence entropy must be continuous at $T = T_c$.

So, $S_A(T_c) = S_B(T_c) \Rightarrow \frac{aT_c^3}{3} + bT_c = \frac{cT_c^3}{3} \Rightarrow T_c = \sqrt{\frac{3b}{c-a}}$

Correct option is (c)

PREVIOUS YEARS SOLUTIONS OF JEST

- Q. The blackbody at a temperature of 6000 K emits a radiation whose intensity spectrum peaks at 600 nm. If the temperature is reduced to 300 K, the spectrum will peak at, [JEST 2015]

(a) 120 μm (b) 12 μm (c) 12 mm (d) 120 mm

Soln. If the blackbody of temperature T emits a radiation whose intensity spectrum peaks at λ_m , then

$$\lambda_m T = \text{constant.}$$

$$\Rightarrow \lambda_{m_1} T_1 = \lambda_{m_2} T_2$$

$$\Rightarrow (600)(6000) = \lambda_{m_2}(300)$$

$$\Rightarrow \lambda_{m_2} = 12000 \text{ nm} = 12 \mu\text{m.}$$

Correct option is (b)

- Q. A thermally insulated ideal gas of volume V_1 and temperature T expands to another enclosure of volume V_2 through a porous plug. What is the change in the temperature of the gas? [JEST 2012]

(a) 0 (b) $T \ln \frac{V_1}{V_2}$ (c) $T \ln \frac{V_2}{V_1}$ (d) $T \ln [(V_2 - V_1)/V_2]$

Soln. When a gas expands through a porous plug, enthalpy remains constant, i.e., $dH = 0$, where $H = U + PV = U + nRT$ (for ideal gas)

Therefore, $dU + nRdT = 0$, where $dU = \frac{f}{2} nRdT$ (for ideal gas).

$$\text{Therefore, } \frac{f}{2} nRdT + nRdT = 0 \Rightarrow dT = 0.$$

Correct option is (a)

- Q. The temperature of a thin bulb filament (assuming that the resistance of the filament is nearly constant) of radius 'r' and length L is proportional to [JEST 2014]

(a) $r^{1/4} L^{-1/2}$ (b) $L^2 r$ (c) $L^{1/4} r^{-1}$ (d) $r^2 L^{-1}$

Soln. The power emitted by a blackbody is $P = \sigma ST^4$ where, $S = 2\pi rL$ and $P = \frac{V^2}{R}$

$$\therefore \frac{V^2}{R} = 2\pi\sigma rLT^4 \Rightarrow \frac{V^2(\pi r^2)}{\rho L} = 2\pi\sigma rLT^4 \Rightarrow T \propto r^{1/4} L^{-1/2}$$

Correct option is (b)

Appendix-i : The Ising Model

The Ising model is an important statistical model which is used to understand the magnetic state of a paramagnetic system by considering the individual spins states that comprise the system. It is assumed that the paramagnetic system is formed by individual spins arranged next to each other. By considering the interaction between these spins we can know about the magnetization state of the paramagnetic system. For simplicity we assume that there is only nearest neighbour interaction between permanent dipole. Under this condition the Hamiltonian of the system can be written as

$$H_i = -\mu_i B \quad (\text{where } \mu \text{ is the magnetic moment of the spin})$$

$$H = -\sum_{i=1}^N \mu_i B - J_1 \sum_{i=1}^N S_i S_{i+1} - J_2 \sum_{i,j} S_i S_j S_k \dots + \dots$$

This is the energy interaction term of three body system

$$\text{part fund } Q_N(V, T) = \sum_s e^{-\beta H}$$

$$A = -kT \ln(Q_N(V, T))$$

In one dimension number of nearest neighbour = 2

In two dimension number of nearest neighbour = 4

In three dimension number of nearest neighbour = 6

In d dimension number of nearest neighbour = 2d

Ising Model in one dimensional:

Consider M dipole if this system is in external magnetic field H.

$$\mu_z = \frac{2q}{2m} S_z, \quad S_z = m_s \hbar, \quad \mu_z = \frac{2q m_s \hbar}{2m} \quad \dots (1)$$

$$H = -B \sum_{i=1}^N \mu_z$$

$$H = -A B \sum_{i=1}^N \sigma_i - J \sum_{i=1}^{N-1} \sigma_i - \sigma_{i+1}; \quad H = -K \sum_{i=1}^N \sigma_i - J \sum_{i=1}^{N-1} \sigma_i - \sigma_{i+1}$$

$$Q_N(V, T) = \sum_{\{\sigma_i\}} e^{-\beta H}; \quad Q_N(V, T) = \sum_{\{\sigma_i\}} e^{+\beta \left[K \sum_{i=1}^N \sigma_i - J \sum_{i=1}^{N-1} \sigma_i - \sigma_{i+1} \right]}$$

In the absence of magnetic field $K=AB$

1st term is zero, $A \times C_i = 0$

$$Q_N(V, T) = \sum_{\{\sigma_i\}} e^{+\beta J \sum_{i=1}^{N-1} \sigma_i - \sigma_{i+1}}$$

Suppose we consider $N=3$ $\left[\begin{matrix} \sigma_i \pm 1 \\ \uparrow \downarrow \end{matrix} \right] (1) \left\{ \begin{matrix} \uparrow \downarrow \\ (-) \end{matrix} \right\}$; $Q_N(V, T) = \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} e^{\beta J \sum_{i=1}^2 \sigma_i - \sigma_{i+1}}$

$$Q_N(V, T) = \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} e^{\beta J (\sigma_1 \sigma_2 + \sigma_2 \sigma_3)}$$

There are only two values for each summation (+1 and -1)



$$Q_N(V, T) = \sum_{\sigma_1} \sum_{\sigma_2} \left[e^{\beta J (\sigma_1 \sigma_2 + \sigma_2 (+1)) + e^{\beta J (\sigma_1 \sigma_2 + \sigma_2 (-1))}} \right]$$

$$Q_N(V, T) = \sum_{\sigma_1} \left[e^{\beta J (\sigma_1 (+1) + (+1) (+1)) + e^{\beta J (\sigma_1 (+1) + (+1) (-1))}} \right] e^{\beta J (\sigma_1 (-1) + (-1) (+1)) + e^{\beta J (\sigma_1 (-1) + (-1) (-1))}}$$

$$\Rightarrow \exp[\beta J (+1) (+1) + (+1) (+1)] + \exp[\beta J (+1) (+1) + (+1) (-1)] \\ + \exp[\beta J (+1) (-1) + (-1) (+1)] + \exp[\beta J (+1) (-1) + (-1) (-1)] \\ + \exp[\beta J (-1) (+1) + (+1) (+1)] + \exp[\beta J (-1) (+1) + (+1) (-1)] \\ + \exp[\beta J (-1) (-1) + (-1) (+1)] + \exp[\beta J (-1) (-1) + (-1) (-1)]$$

$$= e^{2\beta J} + e^0 + e^{-2\beta J} + e^0 + e^{-2\beta J} + e^0 + e^{2\beta J} = 2[e^{2\beta J} + e^{-2\beta J} + 2] = 2(e^{\beta J} + e^{-\beta J})^2 = 2[2 \cosh(\beta J)]^2$$

$$Q_3(V, T) = 2^2 \times 2 (\cosh \beta J)^{3-1} = 2^3 [\cosh \beta J]^{3-1}$$

Similarly for two particles

$$H = Q_N(V, T)_2 \sum_{\sigma_1} \sum_{\sigma_2} e^{\beta J \sum_{i,j} \sigma_i \sigma_j} = \sum_{\sigma_1 \sigma_2} [e^{\beta J (\sigma_1 \sigma_2)}] = e^{\beta J (\sigma_1 (+1))} + e^{\beta J (\sigma_1 (-1))}$$

$$= e^{\beta J (+1)(+1)} + e^{\beta J (+1)(-1)} + e^{\beta J (-1)(+1)} + e^{\beta J (-1)(-1)} = 2[e^{\beta J} + e^{-\beta J}]$$

$$Q_2(V, T) = 2^2 [\cosh \beta J]$$

For N dipole

$$Q_N(V, T) = 2^N (\cosh \beta J)^{N-1}$$

$$A = -k_B T \ln Q_N(V, T) = -k_B T \ln 2^N [\cosh(\beta J)]^{N-1}$$

$$= -k_B T [N \ln 2 + (N-1) \ln \cosh(\beta J)] = -k_B T [N \ln 2 - (N-1) kT \ln \cosh(\beta J)]$$

$$A = -Nk_B T \left[\ln 2 + \left(\frac{N-1}{N} \right) \ln \cosh(\beta J) \right] \text{ if } N \rightarrow \infty$$

$$A = -Nk_B T [\ln 2 + \ln \cosh(\beta J)]$$

$$A = -Nk_B T \ln [2 \cosh \beta J] \quad \dots(i)$$

$$S = -\frac{\partial A}{\partial T} \quad [\beta \text{ is also the function of } T]$$

we can calculate all the properties with the help of value of A.

$$\text{if } B \neq 0 \Rightarrow Q_N(V, T) = 2^N (\cosh \beta J)^{N-1} (2 \cosh \beta \epsilon)^N$$



Q. Consider a system of two Ising spins S_1 and S_2 taking values ± 1 with interaction energy given by $\epsilon = -JS_1S_2$, when it is in thermal equilibrium at temperature T for larger T , the average energy of the system varies as $\frac{C}{k_B T}$, find the value of C .

Soln. $\epsilon_1 = -J(g_1 = 2)$, $\epsilon_2 = +J(g_2 = 2)$

$$\langle E \rangle = \frac{\sum_r g_r E_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}} = \frac{2(-J)e^{\beta J} + 2(J)e^{-\beta J}}{2e^{\beta J} + 2e^{-\beta J}} = \frac{-J[e^{\beta J} - e^{-\beta J}]}{e^{\beta J} + e^{-\beta J}}$$

For large temperature β is very small

$$\langle E \rangle = \frac{-J[1 + \beta J - 1 + \beta J]}{[1 + \beta J + 1 - \beta J]}$$

(neglecting higher order terms)

$$\langle E \rangle = -J \frac{2\beta J}{2} = -\beta J^2 = -\frac{J^2}{k_B T}$$

Comparing this with $\frac{C}{k_B T}$

$$\Rightarrow C = -J^2$$

Appendix-ii : Summary of key points

1. Thermodynamic Limit

If $N \rightarrow \infty$ $V \rightarrow \infty$

Then particle density $n = \frac{N}{V}$ = fixed at a preassigned value

2. Extensive property $\rightarrow N, V, E, S, A$

Intensive property $\rightarrow P, T, \mu$

3. Relation between thermodynamics & statistical mechanics or Boltzmann entropy probability relation

$$S = k_B \log \Omega = -k_B \sum_r P_r \ln P_r$$

Where $\Omega \rightarrow$ number of microstate for a given macrostate.

4. The probability in which r particle in state A and $N-r$ particle in state B is $= \frac{N!}{r!(N-r)!} (P)^r (1-P)^{N-r}$

5. The no. of microstate for N no. of spin S particle is $= (2S+1)^N$

6. The probability of getting a microstate in which there are r particle out of N spin $\frac{1}{2}$ particle in spin up state

$$= N C_r \times \frac{1}{2^N}$$

7. The entropy for classical ideal gas $S = N k_B \ln \left(\frac{V}{h^3} \right) \left(\frac{4\pi m E}{3N/2} \right)^{3/2} + \frac{3}{2} N k_B$

$$\text{or } S = N k_B \ln V + \frac{3}{2} N k_B \left[1 + \ln \frac{2\pi m T k_B}{h^2} \right]$$

8. Sackur tetrode eqn (The eqn that satisfy entropy is an extensive property)

$$S = N k_B \ln V + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

9. Volume of phase Cell $= h^f$

Dimension of phase space $= 2Nf$

$f \rightarrow$ degree of freedom $N \rightarrow$ no. of particles

No. of microstate in phase space $= \frac{\text{Total Volume of phase space allowed to the system}}{\text{Volume of phase cell}}$

$$10. P_r = \frac{g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}$$

11. Partition function for Q.M system (energy discontinuous)

$$Q_N(V, T) = \sum_r g_r e^{-\beta E_r}$$



12. Partition function for classical distinguishable system

$$Q_N(V, T) = \frac{1}{h^{3N}} \int e^{-\beta E_r} d^3p d^3q$$

13. Partition function for classical indistinguishable system

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta E_r} d^3p d^3q$$

14. $Q_N(V, T) = [Q_1(V, T)]^N \rightarrow$ for distinguishable

$$= \frac{1}{N!} [Q_1(V, T)]^N \rightarrow \text{for indistinguishable.}$$

15. Average energy or internal energy

$$U = \langle E_r \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \ln Q_N(V, T)$$

16. $A = U - TS \Rightarrow dA = dU - TdS - SdT \Rightarrow dA = TdS - PdV + \mu dN - TdS - SdT$

$$dA = \mu dN - PdV - SdT$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N, T} \quad S = -\left(\frac{\partial A}{\partial T}\right)_{N, V} \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{T, V}$$

17. Internal energy or average energy

$$U = -T^2 \frac{\partial}{\partial T} \left(\frac{A}{T} \right)_{N, V} = \frac{\partial}{\partial \beta} \left(\frac{A}{kT} \right)_{N, V} = -\frac{\partial}{\partial \beta} \ln Q_N(V, T)$$

18. Helmholtz free energy

$$A = -k_B T \ln Q_N(V, T)$$

19. Specific heat

$$C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_{N, V}$$

Appendix-iii : Miscellaneous solved examples

Q. Obtain an expression for the specific heat capacity of a solid on the basis of Einstein's theory. How far do the results from these theories agree's with experimental data?

Soln. Einstein in 1907 applied quantum principle to the thermal vibration of atoms in solids.

He consider a solid of N_A atom (per kg mole of substance) to behave as $3 N_A$ independent harmonic ascillators each of frequency ν

Quantum theory assumes that atoms are again identical independent harmonic ascillators all of which vibrate independently with the same natural frequency but have discrete energy vaues. These discrete energy values are given by Planck's formula

$$E = n h \nu = n \hbar \omega \quad \dots (i)$$

If dN oscillators have energies lying between E & $E + dE$ then the mean energy of the atomic oscillator is given by

$$\bar{E} = \frac{\sum E dN}{\sum dN} \quad \dots (ii)$$

From statistical mechanics one knows that the number of atomic oscillators dN having energies lying between E & $E + dE$ at temperature T is proportional to $e^{-E/k_B T}$

$$\begin{aligned} \bar{E} &= \frac{\sum_{n=0}^{\infty} n h \nu e^{-n h \nu / k_B T}}{\sum_{n=0}^{\infty} e^{-n h \nu / k_B T}} \\ &= \frac{h \nu [e^{-h \nu / k_B T} + 2e^{-2h \nu / k_B T} + 3e^{-3h \nu / k_B T} + \dots \infty \text{ terms}]}{1 + e^{-h \nu / k_B T} + e^{-2h \nu / k_B T} + e^{-3h \nu / k_B T} + \dots \infty \text{ terms}} \end{aligned}$$

Put $X = -h \nu / k_B T$

$$\begin{aligned} \bar{E} &= \frac{h \nu (e^X + 2e^{2X} + 3e^{3X} + \dots)}{(1 + e^X + e^{2X} + \dots)} \\ &= h \nu \left[\frac{d}{dx} \log (1 + e^X + e^{2X} + \dots \infty \text{ term}) \right] \\ &= h \nu \left[\frac{d}{dx} \log \frac{1}{1 - e^X} \right] = h \nu \left[\frac{d}{dx} [\log 1 - \log (1 - e^X)] \right] \\ &= h \nu \left[- \frac{(-e^X)}{1 - e^X} \right] = h \nu \frac{e^X}{1 - e^X} = h \nu \frac{1}{e^{-X} (1 - e^X)} \\ &= h \nu \frac{1}{e^{-X} - 1} = h \nu \frac{1}{\left(e^{\frac{h \nu}{k_B T}} - 1 \right)} \quad \dots (iii) \end{aligned}$$

The total internal energy of a kg mole of a solid therefore becomes

$$U = 3 N_A \bar{E} = \frac{3 N_A h \nu}{e^{\frac{h \nu}{k_B T}} - 1}$$



and the molar specific heat is $C_V = \frac{dU}{dT} = \frac{-3N_A h\nu e^{\frac{h\nu}{k_B T}} \left(-\frac{h\nu}{k_B T^2} \right)}{\left(e^{\frac{h\nu}{k_B T}} - 1 \right)^2}$

$$C_V = \frac{3N_A k \left(\frac{h\nu}{k_B T} \right)^2 e^{\frac{h\nu}{k_B T}}}{\left(e^{\frac{h\nu}{k_B T}} - 1 \right)^2} = 3R \left(\frac{h\nu}{k_B T} \right)^2 \frac{e^{\frac{h\nu}{k_B T}}}{\left(e^{\frac{h\nu}{k_B T}} - 1 \right)^2} \quad \dots (iv)$$

Case - I → At high temperature $h\nu < k_B T$

Let $x = \frac{h\nu}{k_B T} \Rightarrow$ eqn (iii) becomes

$$\bar{E} = \frac{h\nu}{1+x-1} = \frac{h\nu}{x} = \frac{h\nu}{h\nu} k_B T = k_B T$$

$$U = 3N_A \bar{E} = 3N_A k_B T = 3RT$$

$$C_V = \frac{dU}{dT} = 3R$$

i.e for large values of T , the expression reduces to classical expression

Case-II: At low temperature $h\nu \gg k_B T$ and hence $\frac{h\nu}{k_B T} \gg 1$ therefore

$$\bar{E} = \frac{h\nu}{e^{\frac{h\nu}{k_B T}}}$$

Thus at low temperature the total energy of a kg mole of a solid is given by

$$U = 3N_A h\nu e^{-\frac{h\nu}{k_B T}}$$

$$C_V = \frac{dU}{dT} = -3N_A h\nu \left[-e^{-\frac{h\nu}{k_B T}} \left(\frac{h\nu}{k_B T^2} \right) \right]$$

$$3N_A k \left[\frac{h\nu}{k_B T} \right]^2 e^{-\frac{h\nu}{k_B T}} = 3R \left(\frac{h\nu}{k_B T} \right)^2 \exp \left(-\frac{h\nu}{k_B T} \right) \quad \dots (v)$$

Equation (v) indicates that at low temperature the exponential term is more important than the $\left(\frac{h\nu}{k_B T} \right)^2$ term in

determining the temperature variation of C_V

Thus with decreasing temperature C_V drops exponentially

$$C_V = 3R \left(\frac{h\nu}{k_B T} \right)^2 \left[1 + \frac{h\nu}{k_B T} + \frac{1}{2!} \left(\frac{h\nu}{k_B T} \right)^2 + \dots \right]$$

As $T \rightarrow 0 \quad C_V = 0$



Atomic specific heat of different element differs only because of characteristic frequency ν . At corresponding temp such that $\frac{\nu}{T}$ are same of the atomic specific heat will be same for different element. Einstein theory is in good agreement with the experimental but in case of some solids it is observed that atomic specific heat at low temp decreases more slowly than predicted by this theory.

Q. What is law of equipartition of energy? Derive this using Maxwell's distribution law of molecular velocity.

Soln. This law is applicable to a system of particles in equilibrium and states that average K.E per particle per degree of freedom is $\frac{1}{2}k_B T$ where k_B - Boltzmann's const $T \rightarrow$ absolute temperature.

Derivation : Maxwell's distribution law

$$dN(\vec{C}) = N \left(\frac{m}{2\pi m k_B T} \right)^{3/2} e^{-m(C_x^2 + C_y^2 + C_z^2)/2k_B T} dC_x dC_y dC_z$$

Where N is the total no. of molecule in the gas and C_x, C_y, C_z are the velocity components. Since each of the three components must have the same velocity distribution, the no. of molecules with velocity component between C_x & $C_x + dC_x$ irrespective of other component is

$$dN(C_x) = N \left(\frac{m}{2\pi m k_B T} \right)^{1/2} e^{-mC_x^2/2k_B T} dC_x$$

The average K.E of a molecule in the x-direction

$$\begin{aligned} \bar{E}_x &= \frac{1}{N} \int \left(\frac{1}{2} m C_x^2 \right) dN(C_x) \\ &= \frac{1}{2} m \left(\frac{m}{2\pi m k_B T} \right)^{1/2} \int_0^\infty e^{-bC_x^2} C_x^2 dx \\ \text{Put } \frac{m}{2k_B T} &= b \\ &= \left[\int_{-\infty}^\infty e^{-bx^2} x^2 dx \right] = \frac{1}{2b} \left(\frac{\pi}{b} \right)^{1/2} \end{aligned}$$

Therefore
$$\bar{E}_x = \frac{m}{4b} = \frac{1}{2} k_B T$$

Similarly
$$\bar{E}_y = \bar{E}_z = \frac{1}{2} k_B T$$

This is valid for each degree of freedom. Each molecule of an ideal gas has three translational degree of freedom and so the average K.E per molecule is $\frac{3}{2}k_B T$.

Q. What is law of equipartition of energy? Use this to show that mean energy of a classical simple harmonic oscillator is $k_B T$. Also state the limitation of this law?

Soln. This law states that if a classical system is in thermal equilibrium at absolute temp T then every independent quadratic term in its energy has a mean value equal to $\frac{1}{2}k_B T$.

For a simple harmonic oscillator



$$F = \frac{p^2}{2m} + \frac{1}{2}kx^2 \quad \dots(1)$$

where k- Force constant

$$E = K.E + P.E$$

Suppose that this oscillator is in equilibrium with a heat reservoir at a temperature T which is very high. So mean energy of the oscillator is

$$\bar{E} = \frac{\int E e^{-\beta E} dx dp_x}{\int e^{-\beta E} dx dp_x} \quad (2) \quad \beta = \frac{1}{k_B T}$$

Using eqn (1) in eqn(2)

$$\begin{aligned} \bar{E} &= \frac{\int \frac{p_x^2}{2m} e^{-\frac{\beta p_x^2}{2m}} dp_x}{\int e^{-\frac{\beta p_x^2}{2m}} dp_x} + \frac{\int \frac{1}{2} kx^2 e^{-\frac{\beta kx^2}{2}} dx}{\int e^{-\frac{\beta kx^2}{2}} dx} \\ &= -\frac{d}{d\beta} \log_e \left[\int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x \right] - \frac{\partial}{\partial \beta} \log \left[\int_{-\infty}^{\infty} e^{-\frac{\beta kx^2}{2}} dx \right] \\ \bar{E} &= -\frac{\partial}{\partial \beta} \left[-\frac{1}{2} \log \beta + \log \int_{-\infty}^{\infty} e^{-\frac{A^2}{2m}} dA \right] - \frac{\partial}{\partial \beta} \left[-\frac{1}{2} \log \beta + \log \int_{-\infty}^{\infty} e^{-\frac{\beta kx^2}{2}} d\beta \right] \end{aligned}$$

where $A = \sqrt{\beta} p_x$ and $A = \sqrt{\beta} x$

$$\text{But } \int_{-\infty}^{\infty} e^{-\frac{A^2}{2m}} dA = 0 = \int_{-\infty}^{\infty} e^{-\frac{\beta^2}{2m}} d\beta$$

$$\text{So } \bar{E} = \frac{-\partial}{\partial \beta} \left[-\frac{1}{2} \log \beta \right] - \frac{-\partial}{\partial \beta} \left[-\frac{1}{2} \log \beta \right]$$

$$= \frac{1}{2\beta} + \frac{1}{2\beta} = k_B T$$

Q. The equation of state of an ideal gas is given by $PV = RT$. Show that

$$\beta = \frac{1}{T} \quad \text{and} \quad Z = \frac{1}{P}$$

(ii) An approximate equation of state of a real gas at moderate pressure is $(V-b) = RT/P$. Where R and b are constant. Show that

$$\beta = \frac{\frac{1}{T}}{1 + \frac{Pb}{RT}} \quad (ii) \quad Z = \frac{\frac{1}{P}}{1 + \frac{Pb}{RT}}, \quad Z = \text{Compressibility}$$

Soln.. β for an ideal gas is defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \dots (1)$$



The eqn of state is $PV = RT$

$$\frac{\partial V}{\partial T} = \frac{R}{P} \quad \text{and} \quad R = \frac{PV}{T}$$

Substituting these value in eqn (1)

$$\beta = \frac{1}{V} \cdot \frac{1}{P} \times \frac{PV}{T} \Rightarrow \beta = \frac{1}{T}$$

(ii) For an ideal gas compressibility $Z = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

$$PV = RT \Rightarrow \left(\frac{\partial V}{\partial P} \right)_T = -\frac{RT}{P^2}$$

$$\text{So } Z = -\frac{1}{V} \times -\frac{RT}{P^2} \Rightarrow \frac{RT}{P^2 V} = \frac{PV}{P^2 V} = \frac{1}{P} \Rightarrow Z = \frac{1}{P}$$

$$P(V-b) = RT$$

$$V = \frac{RT}{P} + b$$

$$\Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{P}{Pb + RT} \cdot \frac{R}{P} \Rightarrow \beta = \frac{R}{Pb + RT}$$

$$\text{Now, } \beta = \frac{\frac{RT}{T}}{RT \left(1 + \frac{Pb}{RT} \right)} = \frac{\frac{RT}{T}}{RT \left(1 + \frac{Pb}{RT} \right)} \Rightarrow \boxed{\beta = \frac{\frac{1}{T}}{1 + \frac{Pb}{RT}}}$$

$$P(V-b) = RT \Rightarrow V = \frac{RT}{P} + b$$

$$\Rightarrow \left(\frac{\partial V}{\partial P} \right)_T = -\frac{RT}{P^2}$$

$$\text{Now, } Z = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \times -\frac{RT}{P^2}$$

$$Z = \frac{P}{RT + Pb} \cdot \frac{RT}{P^2} = \frac{RT}{P(RT + Pb)}$$

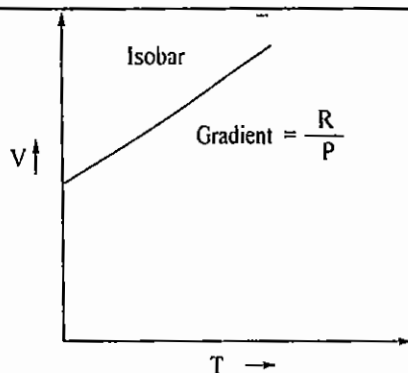
$$\boxed{Z = \frac{\frac{1}{P}}{1 + \frac{Pb}{RT}}}$$

Q. A gas obeys the equation of state $P(V-b) = RT$ where b is a constant for this gas sketch

- (i) a Plot of V versus T at constant P (isobar)
- (ii) a plot of P versus V at constant T (isotherm)
- (iii) a plot of P versus T at constant V (isochore)

Soln. $P = \text{constant}$ then the equation of state $P(V-b) = RT$ can be written

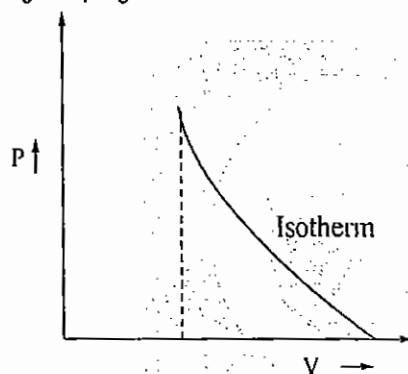
$$V-b = \frac{RT}{P} = \frac{RT}{\text{Constant}} \Rightarrow V = \frac{RT}{\text{Constant}} + b$$



This shows that when $T=0$ $V=b$. Then the plot of V versus T is a straight line with gradient $\frac{R}{P}$ and intercept b as shown in fig.

(ii) If T is constant (isotherm) the eqn of state can be written

$$P = \frac{RT}{V-b} = \frac{\text{const}}{V-b}$$



(Since R and T both are constant)

$$\text{So } P \propto \frac{1}{V-b}$$

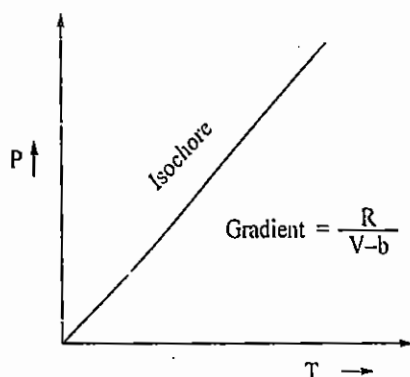
It can easily be seen that when $V \rightarrow \infty$, $P \rightarrow 0$ and when $V \rightarrow b$, $P \rightarrow \infty$. Thus the curve is as shown in fig.

(iii) If V is constant (Isochore) $\Rightarrow P = \frac{RT}{V-b} = \frac{RT}{\text{const}}$

(since V and b are const)

when $T=0 \Rightarrow P=0$

$V=b \Rightarrow P=\infty$



So the plot of P versus T is a straight line with gradient $\frac{R}{V-b}$ and zero intercept as shown.



Q. What is Einstein quantum theory of specific heat? Discuss its limitation.

Soln. Einstein applied Planck's quantum theory to specific heats of solids. In this the average energy of an oscillator per degree of freedom is

$$U = E = \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad \text{for } N \text{ atoms that will be } 3N \text{ degree of freedom}$$

Hence
$$U = E = \frac{3N h\nu}{e^{h\nu/k_B T} - 1}$$

and molar specific heat
$$C_V = \frac{dU}{dT} = \frac{3N h\nu e^{h\nu/k_B T} \left(\frac{-h\nu}{k_B T^2} \right)}{\left(e^{h\nu/k_B T} - 1 \right)^2}$$

$$C_V = \frac{3N k_B e^{h\nu/k_B T} \left(\frac{h\nu}{k_B T} \right)^2}{\left(e^{h\nu/k_B T} - 1 \right)^2} = 3R \left(\frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{\left(e^{h\nu/k_B T} - 1 \right)^2}$$

If $\frac{h\nu}{k_B} = \theta_E$,
$$C_V = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1 \right)^2} \quad \dots (1)$$

where $\theta_E = \frac{h\nu}{k_B}$ is known as Einstein's Characteristic temperature

Case-1 : At high temp $T \gg \theta_E$

we have $\frac{\theta_E}{T} \ll 1$ so that $e^{\theta_E/T} = 1 + \frac{\theta_E}{T}$

so eqn (1) become $C_V = 3R$

This is in agreement with Dulong Petit's law

Case-2: At low temp $T \ll \theta_E$

we have $\frac{\theta_E}{T} \gg 1$ so that $e^{\theta_E/T} \gg 1$

so eqn (1) become

$$C_V = 3R \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad \dots (2)$$

This show that as $T \rightarrow 0$ the specific heat C_V also approach to zero

Limitation : - The theory fails at very low temp where C_V is found to be nearly proportional to T^3 rather than as given by eqn (3). This is due to neglecting the mutual forces exerted by the atom upon one another.

Q. Show that if f is the Fermi-Dirac distribution function is a maximum at the fermi level, Also show that $-\frac{\partial f}{\partial E}$ is symmetric about the Fermi-level.

Soln. We have $f = \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}} = \frac{1}{1 + e^x}$ where, $x = \frac{E - E_F}{k_B T}$, $E_F \rightarrow$ Fermi level

Now
$$\frac{\partial f}{\partial E} = \frac{\partial f}{\partial x} \cdot \frac{\partial x}{\partial E} = -\frac{e^x}{(1 + e^x)^2} \cdot \frac{1}{k_B T} \cdot \frac{\partial f}{\partial E} = \frac{1}{k_B T} \frac{e^x}{(1 + e^x)^2}$$



$$\text{and } -\frac{\partial^2 f}{\partial E} = -\frac{d}{dx} \left[\left(\frac{\partial f}{\partial E} \right) \frac{\partial x}{\partial E} \right] = \frac{1}{k_B T} \frac{d}{dx} \left(-\frac{\partial f}{\partial E} \right) = \frac{1}{(k_B T)^2} \frac{(1+e^x)^2 e^x - 2e^x (1+e^x) e^x}{(1+e^x)^4}$$

$$-\frac{\partial f}{\partial E} \text{ is a maximum when } -\frac{\partial^2 f}{\partial E^2} = 0$$

$$(1+e^x)^2 - 2e^x (1+e^x) = 0$$

$$(1+e^x) [1+e^x - 2e^x] = 0$$

$$(1+e^x) (1-e^x) = 0$$

$$1-e^{2x} = 0$$

$$e^{2x} = 1 = e^0 \Rightarrow x = 0$$

$$x = \frac{E - E_F}{k_B T} = 0 \Rightarrow E = E_F$$

Thus $-\frac{\partial f}{\partial E}$ is a maximum at the fermi level

If E is below E_F by the same amount, x is replaced by $(-x)$

$$\text{Then } -\frac{\partial f}{\partial E} = \frac{1}{k_B T} \frac{e^{-x}}{(1+e^{-x})^2} = \frac{1}{k_B T} \frac{e^x}{(1+e^x)^2}$$

$$\left(\frac{e^{-x}}{(1+e^{-x})^2} = \frac{e^{2x} \times e^{-x}}{e^{2x} (1+e^{-2x} + 2e^{-x})} = \frac{e^x}{e^{2x} + 1 + 2e^x} = \frac{e^x}{(1+e^x)^2} \right)$$

Thus $-\frac{\partial f}{\partial E}$ is unchanged upon the reversal of the sign of x

Hence $-\frac{\partial f}{\partial E}$ is symmetric about $x=0$ i.e. about $E = E_F$

- Q.** By considering the variation of E_F with volume show that there is a relation between pressure and volume of the free electron gas $PV = 2/3 U$, where U is the internal energy of the gas at zero Kelvin. Hence show that the isothermal elasticity of the electron gas is $\beta = 9V/10U$ free particle is represented by a plane wave e^{ikr} .

Soln.. The general expression for energy is $U = \frac{\hbar^2 K^2}{2m} \rightarrow$ energy of free particle with $Kr = \text{constant}$ (say α)

$$\text{Volume } V = br^3 \text{ with } b = \text{constant} = \frac{4}{3}\pi$$

$$\text{Thus } U = \frac{\hbar^2}{2m} \left(\frac{\alpha^2}{r^2} \right) = \frac{\hbar^2 \alpha^2}{2m} \left(\frac{b}{V} \right)^{2/3} \quad \dots (1)$$

Differentiating equation (1) w.r.t V we get

$$\frac{dU}{dV} = \frac{\hbar^2 \alpha^2}{2m} b^{2/3} \left(\frac{-2}{3} \frac{1}{V^{5/3}} \right)$$



we know that, $P = -\left(\frac{dU}{dV}\right)$... (2)

Thus, $P = \frac{h^2 \alpha^2}{2m} b^{2/3} \frac{2}{3} \left(\frac{1}{V^{2/3}}\right) \left(\frac{1}{V}\right)$

So $PV = \frac{h^2 \alpha^2 b^{2/3}}{2m} \frac{2}{3} \frac{1}{V^{2/3}} = \frac{2}{3} \frac{h^2 \alpha^2}{2m} \left(\frac{b}{V}\right)^{2/3}$

$$\boxed{PV = \frac{2}{3} U} \quad \dots (3)$$

Now differentiating equation (3) we get

$$P + V \left(\frac{dP}{dV}\right) = \frac{2}{3} \frac{dU}{dV}$$

Using equation (2)

$$P + V \left(\frac{dP}{dV}\right) = \frac{2}{3} \times (-P)$$

$$V \frac{dP}{dV} = -\frac{5}{3} P \Rightarrow -\frac{dV}{V dP} = \frac{3}{5P}$$

Isothermal elasticity $B = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)$

$$B = \frac{3}{5P}$$

From eqn 3 $P = \frac{2}{3} \frac{U}{V} \Rightarrow \frac{1}{P} = \frac{3V}{2U}$

So $B = \frac{3}{5} \times \frac{3V}{2U} = \frac{9V}{10U}$

- Q.** In a system of two particles each particle can be in any one of three possible quantum state. Find the ratio of the probability that the two particles occupy the same state to the probability that the two particles occupy different states for MB, BE and ED statistics

Soln.. Let r be the desired ratio

$W_1 \rightarrow$ the number of ways in which two particles can occupy same state

$W_2 \rightarrow$ The state in which they occupy different state then

$$r = \frac{W_1}{W_2}$$

For MB Statistics :

The particles are distinguishable and $W_1 = 3$

Now one particle can be in any one of the 3 quantum state and remaining particles can be in any one of the 2 quantum state that are available to it. So



$$W_2 = 3 \times 2 = 6$$

$$\text{Therefore } r = \frac{W_1}{W_2} = \frac{3}{6} = \frac{1}{2}$$

For FD statistics :

The particles are indistinguishable, $W_1 = 0$. Since the two particles can't be in the same quantum state

$$\text{Here } W_2 = {}^3C_2 = 3$$

$$\text{So } r = \frac{W_1}{W_2} = \frac{0}{3} = 0$$

For BE statistics : Again the particles are indistinguishable

$$W_1 = 3 \text{ and } W_2 = {}^3C_2 = 3$$

$$\text{So } r = \frac{W_1}{W_2} = \frac{3}{3} = 1$$

Q. Show that for a two dimensional electron gas the number of electrons per unit area is given by

$$n = \frac{4\pi mk_B T}{h^2} \ln \left(e^{\frac{E_F}{k_B T}} + 1 \right)$$

Soln.. The density of state function for a two dimensional electron gas is given by

$$g(E)dE = \frac{2A}{h^2} (2\pi p dp) = \frac{4\pi mA}{h^2} dE$$

$$\left(\because E = \frac{p^2}{2m} \Rightarrow p^2 = 2mE \text{ so } 2p dp = 2m dE \right)$$

$A \rightarrow$ Area of two dimensional container, $m =$ mass of electron

The number of electron is

$$N = \int_0^\infty g(E)f(E)dE = \frac{4\pi mA}{h^2} \int_0^\infty \frac{dE}{1 + e^{\frac{E-E_F}{k_B T}}}$$

The number of electrons per unit area is given by

$$n = \frac{N}{A} = \frac{4\pi mk_B T}{h^2} \int_0^\infty \frac{dx}{1 + e^{x-\eta}}$$

where $x = \frac{E}{k_B T} \Rightarrow dx = \frac{dE}{k_B T}$ and $\eta = \frac{E_F}{k_B T}$

Now the integral $I = \int_0^\infty \frac{dx}{1 + e^{x-\eta}} = \int_0^\infty \frac{e^{-x} dx}{e^{-x} + e^{-\eta}}$



Substituting $Z = e^{-x} + e^{-\eta} \Rightarrow dZ = -e^{-x} dx$

$$\text{So } I = \int_{e^{-\eta}}^{1+e^{-\eta}} \frac{dZ}{Z} = \ln \left(\frac{1+e^{-\eta}}{e^{-\eta}} \right) = \ln (1+e^{+\eta})$$

$$\text{So } n = \frac{4\pi m k_B T}{h^2} \ln \left(1 + e^{\frac{E_F}{k_B T}} \right)$$

Q. The earth receives $2.0 \text{ cal cm}^{-2} \text{ min}^{-1}$ from the sun. If angular diameter of the sun is $32'$ and is treated as a black body, deduce its surface temperature.

Given: $\sigma = 5.7 \times 10^{-12} \text{ watt cm}^{-2} \text{ K}^{-4}$?

Soln. As $T^4 = \frac{S}{\sigma} \left(\frac{R}{r} \right)^2$

Solar constant $S = \frac{2}{60} \text{ cal cm}^{-2} \text{ min}^{-1}$

$$= \frac{2 \times 4.2}{60} \text{ joule} \times (10^{-2} \text{ m})^{-2} \times \text{min}^{-1}$$

$$= 14 \times 10^2 \text{ joule m}^{-2} \text{ min}^{-1}$$

$$\left(\frac{r}{R} \right) = \frac{\text{radius of the sun}}{\text{distance of the earth from the sun}}$$

Angular diameter = $32'$

$$\text{angular radius} = \frac{r}{R} = \frac{32'}{2} = 16' = \left(\frac{16}{60} \right)^\circ$$

$$= \frac{16}{60} = \frac{\pi}{180} \text{ radian}$$

$$\frac{R}{r} = \frac{180 \times 60}{16 \times \pi}$$

Thus $T^4 = \frac{14 \times 10^2}{\sigma} \times \left(\frac{180 \times 60}{16 \pi} \right)^2$

$$= \frac{14 \times 10^2}{5.7 \times 10^{-8}} \times \left(\frac{180 \times 60}{16 \pi} \right)^2$$

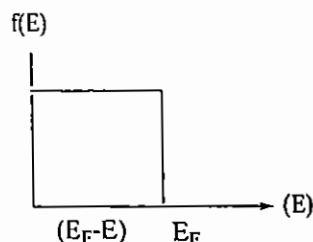
$$\Rightarrow \boxed{T = 5803 \text{ K}}$$

$$\begin{cases} \sin \sigma = 5.7 \times 10^{-12} \text{ watt cm}^{-2} \text{ K}^{-4} \\ = 5.7 \times 10^{-8} \text{ watt m}^{-2} \text{ K}^{-4} \end{cases}$$

Q. Show that a fraction of \bar{e} in free \bar{e} gas at $T = 0 \text{ K}$ between $(E_F - E)$ and E_F ($E \ll E_F$) is $\frac{3E}{2E_F}$?

$$N = \int_0^{E_F} g(E) f(E) dE$$

Soln. Since $g(p) dp = \frac{4\pi V}{h^3} p^2 dp$





$$\begin{aligned}
 g(E)dE &= \frac{4\pi V}{h^3} \cdot p^2 \cdot \frac{m}{p} dE \\
 &= \frac{4\pi V}{h^3} (\sqrt{2mE}) \cdot m dE \\
 &= \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE \\
 &= A E^{1/2} dE
 \end{aligned}
 \quad \left[\begin{array}{l} \text{As } p^2 = 2mE \\ \Rightarrow 2p dp = 2m dE \\ \Rightarrow dp = \frac{m}{p} dE \end{array} \right]$$

$$N = A \int_0^{E_F} E^{1/2} dE = A \cdot \frac{2}{3} E_F^{3/2}$$

No. density of states upto $E_F - \epsilon$

$$N' = A \int_0^{E_F - \epsilon} E^{1/2} dE = A \cdot \frac{2}{3} (E_F - \epsilon)^{3/2}$$

$$\text{fraction of } \bar{\epsilon} = \frac{N - N'}{N} = \frac{E_F^{3/2} - (E_F - \epsilon)^{3/2}}{(E_F)^{3/2}} = \frac{E_F^{3/2} - E_F^{3/2} \left(1 - \frac{\epsilon}{E_F}\right)^{3/2}}{(E_F)^{3/2}} = 1 - \left(1 - \frac{3}{2} \frac{\epsilon}{E_F}\right)$$

$$\Rightarrow \boxed{\frac{N - N'}{N} = \frac{3}{2} \frac{\epsilon}{E_F}}$$

Q. N particles obey M.B statistics are distributed among three states having energy $\epsilon_1 = 0, \epsilon_2 = k_B T$ and $\epsilon_3 = 2k_B T$. If total equilibrium energy of the system is $1000 k_B T$. What is value of N ?

Soln. Since

number of particles energy

$$\begin{array}{lcl}
 N_1 + N_2 + N_3 = N & N_3 & \xrightarrow{\text{(iii)}} 2k_B T \\
 \text{Now } \frac{N_1}{N_2} = \frac{e^{-\beta \epsilon_1}}{e^{-\beta \epsilon_2}} & N_2 & \xrightarrow{\text{(ii)}} k_B T \\
 & N_1 & \xrightarrow{\text{(i) state}} 0
 \end{array}$$

$$\Rightarrow N_1 = N_2 e^{-\beta(\epsilon_1 - \epsilon_2)} \quad \dots (1)$$

$$\text{Similarly } N_2 = N_3 e^{-\beta(\epsilon_2 - \epsilon_3)} \quad \dots (2)$$

$$\text{from (1) } N_1 = N_2 e^{\frac{(0 - k_B T)}{k_B T}} = N_2 e^{-1}, \quad \left\{ \beta = \frac{1}{k_B T} \right.$$

$$\begin{aligned}
 N_3 &= N_2 e^{\frac{(k_B T) - 2k_B T}{k_B T}} \\
 &= N_2 e^{-1}
 \end{aligned}$$



$$\begin{aligned}
 \text{Thus } N &= N_1 + N_2 + N_3 \\
 &= N_2 e + N_2 + N_2 e^{-1} \\
 &= N_2 \left(e + 1 + \frac{1}{e} \right) \quad \dots (3)
 \end{aligned}$$

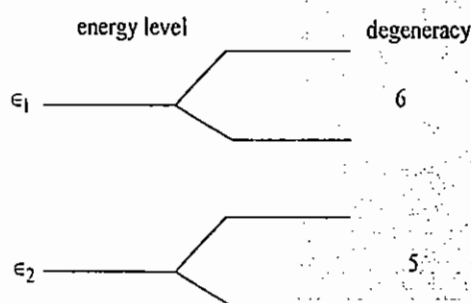
$$\begin{aligned}
 \text{As } 1000 k_B T &= 0 + k_B T N_2 + 2k_B T N_3 \\
 \Rightarrow 1000 &= N_2 + 2N_2 e^{-1} \quad \dots (4)
 \end{aligned}$$

from (3) and (4)

$$\begin{aligned}
 \frac{N}{1000} &= \frac{e + 1 + e^{-1}}{1 + 2e^{-1}} = 2.354 \\
 &= N = 2354 \approx 2400
 \end{aligned}$$

Q. Four identical fermions are to be distributed in energy level ϵ_2 is 6 fold degenerate. Find the energy corresponding to the distribution having maximum number of arrangement.

Soln. The no. of ways in which particles can be distributed is
 $(4, 0), (0, 4), (1, 3), (3, 1), (2, 2)$



$$\text{Total no. of ways } \Omega = \left(\frac{g_1}{n_1(g_1 - n_1)} \right) \times \left(\frac{g_2}{n_2(g_2 - n_2)} \right)_{\epsilon_2}$$

$$\Omega_{4,0} = \frac{5}{4(5-4)} \times \frac{6}{0(6)} = 5$$

$$\Omega_{0,4} = \frac{5}{0(5)} \times \frac{6}{4(6-4)} = 15$$

$$\Omega_{3,1} = \frac{5}{3(2)} \times \frac{6}{1(5)} = 60$$

$$\Omega_{1,3} = \frac{5}{1(4)} \times \frac{6}{3(3)} = 100$$

$$\Omega_{2,2} = \frac{5}{2(3)} \times \frac{6}{2(4)} = 150$$

Energy having maximum no. of arrangements = $2\epsilon_1 + 2\epsilon_2$

References

*The following books have been referred to while preparing this booklet.
The authors of this booklet owe credits to all of them.*

- | | | |
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R.H. Dittman |
| Fundamentals of Statistical
& Thermal Physics | – | F. Rief |
| An introductory course of
Statistical Mechanics | – | Palash B Pal |
| Statistical & Thermal Physics
An Introduction | – | S. Lokanathan,
R.S. Gambhir |
| Statistical Mechanics | – | R.K. Patharia |

*For the students interest, they can refer to the following books for
further reading.*

- | | | |
|--|---|-----------------------|
| Statistical Mechanics | – | Kerson Huang |
| Thermal Physics | – | Charles Kittel |
| A Treatise on Heat | – | Saha & Srivastava |
| Engineering Thermodynamics | – | P.K. Nag |
| Thermodynamics | – | Garg, Bansal & Ghosh |
| Heat & Thermodynamics | – | H.P. Roy & A.B. Gupta |
| Heat Thermodynamics &
Statistical Physics | – | Brijlal & Subramanyam |