

Kinetic Theory of Gas

17.02.14

Atomic theory of Dalton (1803)

Atom makes the gas particles

> Gas molecules move randomly in available space.

Postulates of KTG:

1. Gas molecules are made of rigid solid sphere which moves randomly in available space
2. The Collision between gas molecules with the walls are Completely elastic
3. There is no force of interaction among gas molecules. They are free particles (Potential, $V=0$)
4. The Size of gas molecules is way less than the average distance between molecules. $x \gg r$
5. Time difference between collision is much more greater than the Collision time
6. The Probability of moving gas molecules in each direction is always equal
7. There is no effect of gravity on gas molecules.

Exerted Pressure of a gas:

Let us now Consider there are N number of gas molecules within the Container $N = \sum n_i$

$$\langle v \rangle = \frac{\sum n_i v_i}{\sum n_i} \quad \vec{v}_i = v_{ix} \hat{i} + v_{iy} \hat{j} + v_{iz} \hat{k}$$

$$v_i^2 = v_{ix}^2 + v_{iy}^2 + v_{iz}^2$$

$$v_{ix} = v_{iy} = v_{iz} = \frac{v^2}{3} \text{ (Equally probable)}$$

Let the size of the Container $L \times L \times L$

$$P_{ix} = m v_{ix}$$

Change in momentum along x direction

$$\Delta P_{ix} = 2mv_{ix}$$

Since force is rate of change in momentum.

$$F_{ix} = n_i \frac{2m\vec{v}_{ix}}{\Delta t} = \frac{2m\vec{v}_{ix} n_i}{(\frac{2L}{\vec{v}_{iz}})}$$

Here $\Delta t = \frac{2L}{\vec{v}_{iz}}$ (Time approximation)

$$F_{ix} = \frac{n_i}{L} m \vec{v}_{ix}$$

Exerted Pressure, $P_{ix} = \frac{F_{ix}}{L^2} = \frac{n_i m \vec{v}_{ix}}{L^3}$

$$P_x = \sum P_{ix} = \frac{m}{L^3} \sum n_i \vec{v}_{ix} = \frac{mN}{L^3} \frac{\sum n_i \vec{v}_{ix}}{\sum n_i} = \frac{mN}{L^3} \langle \vec{v}_x^2 \rangle$$

Also we have, $\langle \vec{v}_x^2 \rangle = \frac{\langle v^2 \rangle}{3}$

So $P_x = \frac{1}{3} \frac{mN}{L^3} \langle v^2 \rangle = \frac{1}{3} \frac{mN}{V} \langle v^2 \rangle = \frac{1}{3} \frac{M}{V} \langle v^2 \rangle$

$$P = \frac{1}{3} \rho \langle v^2 \rangle \Rightarrow \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3P}{\rho}}$$

Root mean square of velocity, $\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3P}{\rho}}$

Velocity of Sound, $V = \sqrt{\frac{3P}{\rho}}$

Average KE of gas molecules, $KE = \frac{1}{2} m \langle v^2 \rangle$

$$P = \frac{1}{3} \frac{N}{V} m \langle v^2 \rangle = \frac{2}{3} N \times \frac{1}{V} \times \frac{1}{2} m \langle v^2 \rangle$$

$$\therefore PV = \frac{2}{3} NE$$

Maxwell's Equipartition Theorem:

The average energy carried by one molecule in one degree of freedom is $\frac{1}{2} k_B T$ (KE)

For f degrees of freedom, $E = f/2 k_B T$

$$PV = \frac{2}{3} NE \times 1 = \frac{2}{3} N \times \frac{3}{2} k_B T = N k_B T \quad (\text{In space } f=3)$$

$$PV = N k_B T$$

xyz

$N = \text{no of molecules}$

$$K_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$N_A = 6.02 \times 10^{23} = 1 \text{ mol}$$

$$n = \frac{N}{N_A} = \frac{\text{No of Particles}}{\text{Avogadro No}}$$

Boyle's law: $PV = NKT$

At $T = \text{constant}$ $P \propto \frac{1}{V}$

Reynault's law:

At $V = \text{constant}$

$$P \propto T$$

$$PV = NK_B T = n N_A K_B T = nRT$$

$$PV = nRT \Rightarrow \text{Ideal gas eqn.}$$

32 gm oxygen molecules

= 1 mol O_2 molecules

$M \Rightarrow \text{Molar mass}$

$m \Rightarrow \text{Mass of one molecule}$

Charles's law:

$$PV = NKT$$

At Constant P, $V \propto T$

18/02/2024:

$$f(-x) = f(x)$$

$$\int_{-a}^a f(x) dx = 2 \int_0^a f(x) dx \Rightarrow \text{Even function}$$

$$f(-x) = -f(x)$$

$$\int_{-a}^a f(x) dx = 0 \Rightarrow \text{odd function}$$

$$\textcircled{1} \quad \int_{-\infty}^{+\infty} x^5 e^{-\alpha x^2} dx = 0$$

x^5 = odd function

$e^{-\alpha x^2}$ = Even function

Symmetric limit

$$\textcircled{2} \quad \int_{-\infty}^{+\infty} x^n e^{-\alpha x^2} dx = \begin{cases} 0 & 1+n = \text{Even function} \\ \frac{1}{\alpha^{\frac{n+1}{2}}} \Gamma\left(\frac{n+1}{2}\right) & 1+n = \text{odd function} \end{cases}$$

> Gamma function:

$$\int_0^{\infty} e^{-x} x^{n-1} dx = \Gamma(n)$$

$$\Gamma(n+1) = n! n$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

Maxwell's Velocity Distribution:

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} 4\pi v^2 dv = f(v) dv \Rightarrow 3D$$

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} 2\pi v dv = f(v) dv \Rightarrow 2D$$

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv^2}{2k_B T}} dv = f(v) dv \Rightarrow 1D$$

$$\langle x \rangle = \frac{\sum x_i p_i}{\sum p_i} = \frac{\int x P(x) dx}{\int P(x) dx}$$

$$\langle x+x^2 \rangle = \frac{\int (x+x^2) P(x) dx}{\int P(x) dx}$$

Limits of v are:

$$2D: 0 \rightarrow \infty$$

$$3D: 0 \rightarrow \infty$$

$$1D: -\infty \rightarrow +\infty$$

Average Velocity of v:

$$\langle v \rangle = \frac{\int_0^\infty v f(v) dv}{\int_0^\infty f(v) dv} = \frac{\int_0^\infty v \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} 4\pi v^2 dv}{\int_0^\infty \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} 4\pi v^2 dv}$$

$$= \frac{\int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv}{\int_0^\infty v^2 e^{-\frac{mv^2}{2k_B T}} dv}$$

$$= \frac{\int_0^\infty e^{-t} \frac{KT}{m} dt}{\int_0^\infty t^2 e^{-t} \frac{KT}{m} dt}$$

$$= \frac{\int_0^\infty e^{-t} \frac{KT}{m} dt}{\int_0^\infty \frac{2KT}{m} t e^{-t} \sqrt{\frac{m}{2KT}} \frac{KT}{m} t^{-1/2} dt}$$

$$\frac{mv^2}{2k_B T} = t$$

$$\Rightarrow v dv = \frac{KT}{m} dt$$

$$\Rightarrow dv = \sqrt{\frac{m}{2KT}} \frac{KT}{m} t^{-1/2} dt$$

$$= \sqrt{\frac{2KT}{m}} \frac{1}{\frac{\sqrt{m}}{2}} = \sqrt{\frac{8KT}{m}}$$

One dimensional Average Velocity:

$$f(v)dv = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} dv$$

$$\langle v \rangle = \frac{\int v f(v) dv}{\int f(v) dv} = \frac{\int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} v dv}{\int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} dv} = 0$$

Average Value of v^2 in 3D:

$$\langle v^2 \rangle = \frac{\int_0^{\infty} f(v) v^2 dv}{\int_0^{\infty} f(v) dv} = \frac{\int_0^{\infty} e^{-\frac{mv^2}{2kT}} v^2 dv}{\int_0^{\infty} e^{-\frac{mv^2}{2kT}} dv} = \frac{3kT}{m}$$

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

In One dimension:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \langle v^2 \rangle / 3$$

$$3 \langle v_x^2 \rangle = \langle v^2 \rangle = \frac{3kT}{m}$$

$$\sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{kT}{m}}$$

Most Probable Velocity:

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2$$

$$\text{for } v = v_{\max} \quad \frac{df(v)}{dv} = 0$$

$$\left[e^{-\frac{mv^2}{2kT}} \left(-\frac{2mv}{2kT} \right) v^2 + e^{-\frac{mv^2}{2kT}} 2v \right] = 0$$

$$\frac{mv}{K_B T} v^2 = 2v \Rightarrow v = \sqrt{\frac{2kT}{m}}$$

$$\text{Most Probable Velocity, } v = \sqrt{\frac{2kT}{m}}$$

Average Value of KE:

$$f(v)dv = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} dv$$

$$\langle \frac{1}{2}mv^2 \rangle = \frac{\int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} \frac{1}{2}mv^2 dv}{\int_{-\infty}^{+\infty} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv^2}{2kT}} dv}$$

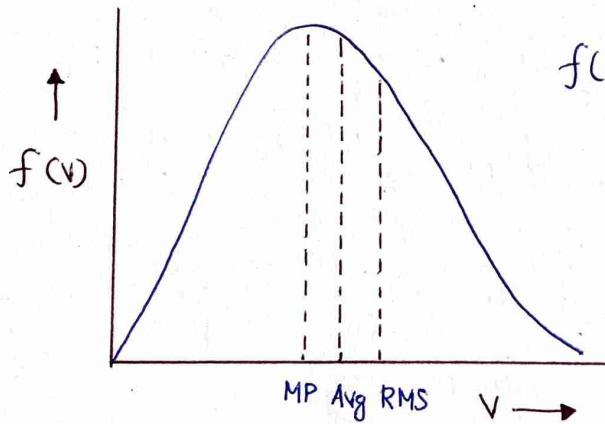
$$= \frac{\frac{1}{2}m \int_{-\infty}^{+\infty} e^{-\frac{mv^2}{2kT}} v^2 dv}{\int_{-\infty}^{+\infty} e^{-\frac{mv^2}{2kT}} dv} = \frac{1}{2}kT$$

$$\langle E \rangle = \frac{1}{2}k_B T \quad (1-D) \quad \langle E \rangle = \frac{3}{2}k_B T \quad (3-D)$$

per degree of freedom, $\langle E \rangle = \frac{f}{2}k_B T$

Graphical Analysis:

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

(Gaussian Curve)

Area of the Curve,

$$\int f(v) dv = 1$$

> If temperature increase, Peak will be shifted to right

$$V_{rms} > V_{avg} > V_{MP}$$

> $C_V = \frac{dU}{dT} \Rightarrow$ Specific heat at Constant Volume

> $C_P = \frac{dQ}{dT} \Rightarrow$ Specific heat at Constant Pressure

$$C_P - C_V = R \quad (\text{Mayer's Formula})$$

Degree of Freedom (f):

Internal energy of single gas molecules having degree of freedom. $U = \frac{f}{2} K_B T N$

$$C_V = \frac{dU}{dT} = \frac{f}{2} K_B N \quad C_P = \left(\frac{f}{2} + 1\right) K_B N$$

$$C_V = \frac{f}{2} R \quad C_P = \left(\frac{f}{2} + 1\right) R$$

$$\text{Ratio of Specific heat, } \gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$$

> No of Square term present in the expression for energy of the Particle \Rightarrow dof

> Monoatomic Gas: He, Ne, Br

$$E = \frac{1}{2} m \ddot{x}^2 + \frac{1}{2} m \ddot{y}^2 + \frac{1}{2} m \ddot{z}^2$$

$$\text{dof} = 3 \quad \gamma = 1 + \frac{2}{3} = 1.67$$

> Diatomic Gas: O₂, N₂, H₂ * For Blackbody

$$\text{Rotation KE} = \frac{1}{2} I \omega^2 \quad \gamma = 4/3$$

$$KE = \frac{1}{2} m (\ddot{x}^2 + \ddot{y}^2 + \ddot{z}^2) + \frac{1}{2} I' \omega_z^2 + \frac{1}{2} I' \omega_y^2$$

$$\text{dof} = 2 + 3 = 5 \quad \gamma = 1 + \frac{2}{5} = 1.4$$

> If temperature increases:

$$E = \frac{1}{2} m (\ddot{x}^2 + \ddot{y}^2 + \ddot{z}^2) + \frac{1}{2} I \omega_z^2 + \frac{1}{2} I' \omega_y^2 + \frac{1}{2} m \ddot{x} + \frac{1}{2} K_{xx}$$

$$\text{dof} = 6 \quad C_V = 3R \quad C_P = 4R \quad \gamma = 4/3$$

Linear triatomic (CO₂) same as diatomic.

① In 2D for monoatomic gas dof = 2

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

Non Linear Gases:

Translational dof = 3

At lower temperature

Rotational dof = 3

$f = 6$

$$E = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{1}{2} I (\omega_x^2 + \omega_y^2 + \omega_z^2)$$

> Translational dof = 3

At Higher

Rotational dof = 3

temperature

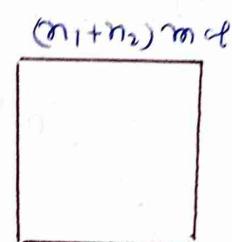
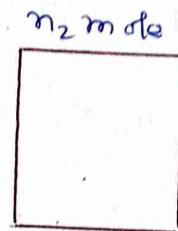
Mode

dof = 1

$f = 7$

Specific heat of Mixture of a gas

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$$dU_1 = n_1 C_{V1} dT$$

$$dU_2 = n_2 C_{V2} dT$$

$$dU_T = (n_1 + n_2) C_{V_{mix}} dT$$

Internal energy is an additive quantity

$$\text{So, } dU_T = dU_1 + dU_2$$

$$\text{or } (n_1 + n_2) C_{V_{mix}} dT = n_1 C_{V1} dT + n_2 C_{V2} dT$$

or

$$C_{V_{mix}} = \frac{n_1 C_{V1} + n_2 C_{V2}}{n_1 + n_2}$$

So,

$$C_{V_{mix}} = \frac{\sum n_i C_{Vi}}{\sum n_i}$$

Similarly, $C_{P_{mix}} = \frac{\sum n_i C_{Pi}}{\sum n_i}$

$$\gamma_{mix} = \frac{\sum n_i C_{Pi}}{\sum n_i C_{Vi}} = 1 + \frac{2}{f_{mix}}$$

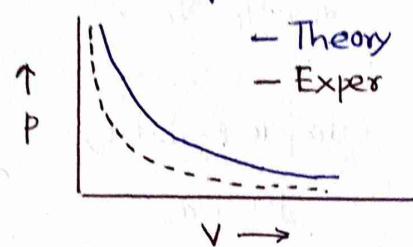
$$f_{\text{mix}} = \frac{n_1 f_1 + n_2 f_2 + n_3 f_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i f_i}{\sum n_i}$$

① Boyle's law:

At Constant temperature $P \propto \frac{1}{V}$

$$P = \frac{K}{V} \Rightarrow PV = K$$

$PV = \text{Constant}$



As temperature increases

experimental curve tends to theoretical curve

Real gas tends to ideal gas

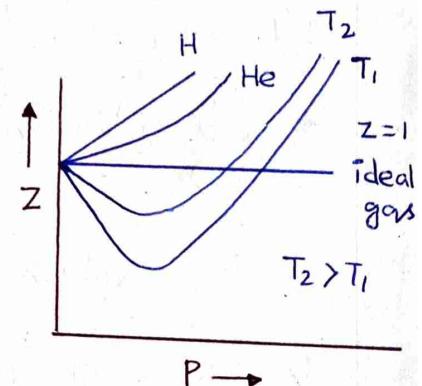
At lower pressure, Real gas tends to ideal gas.

② Compressibility Factor:

For 1 mole gas, $Z = \frac{PV}{RT}$

Ideal gas: $PV = RT$ then $Z = 1$

Real gas: $PV \neq RT$ so, $Z \neq 1$



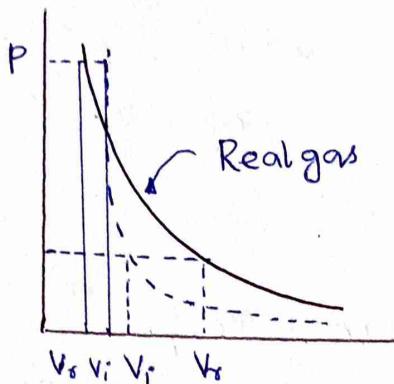
As temperature increase Curve goes to ideal curve
at $Z=1$ Real gas tends to ideal gas.

Ideal Gas

- ① Postulates are followed
- ② $PV = nRT$
- ③ $Z = 1$
- ④ There are no interaction between gas molecules
- ⑤ They have no fixed volume

Real Gas

- ② Postulates are not followed.
- ② $PV \neq nRT$
- ③ $Z \neq 1$
- ④ There are interaction between gas molecules.
- ⑤ They doesn't have any fixed volume



At Constant P and T

$V_{\text{ideal}} > V_{\text{real}}$

(Negative deviation)

$V_{\text{ideal}} < V_{\text{real}}$

(Positive deviation)

Compressibility factor

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

For ideal gas

$$V_{\text{ideal}} = 22.4 L$$

If $V_{\text{real}} > 22.4 L \Rightarrow Z > 1$ (Less compressible)

Water is less compressible and air is more.

> Ideal gas cannot be liquified.

$$Z = 1$$

$$Z > 1$$

$$Z < 1$$

$$g_{\text{ideal}}$$

Gas expand

$$V_{\text{real}} < V_{\text{ideal}}$$

$$g_{\text{gas}}$$

(Repulsion)

(Gas compressed)

$$PV = nRT$$

$$V_{\text{real}} > V_{\text{ideal}}$$

• STP Condition: At standard temperature, pressure

$$T = 273 K, P = 1 \text{ atm}$$

$$\text{volume} = 22.4 \text{ Ltr}$$

At STP the volume of a gas is 22.4 Ltr

=) Here, $V_{\text{real}} > V_{\text{ideal}}$

$$22.4 L > 22.4 L$$

Repulsive in Nature

Positive deviation

No liquification

$$Z > 1$$

So gas
Expands.

$$> PV = \frac{1}{3} m N \langle v^2 \rangle = \frac{2}{3} \left[\frac{1}{2} M \langle v^2 \rangle \right] = \frac{2}{3} U$$

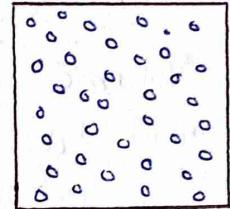
$$\frac{U}{V} = \frac{3}{2} P \Rightarrow \text{Energy density} = \frac{3}{2} P$$

> For 1 mole of real gas Van der waals equation is given by

$$(P + \frac{na}{V^2})(V - nb) = nRT \quad (n \text{ mole})$$

$$(P + \frac{a}{V^2})(V - b) = RT \quad (1 \text{ mole})$$

Ideal gas has negligible volume so the available volume for movement is equal to the volume of container.



But for real gas, the available volume $= (V - nb)$
 'nb' is volume correction term and b depends on the radius of gas molecules.

$$\text{Pressure Correction. } \Delta P \propto (\frac{n}{V})^2 \Rightarrow \Delta P = a(\frac{n}{V})^2$$

$$P_{\text{real}} < P_{\text{ideal}}$$

$$P_{\text{real}} = P_{\text{ideal}} - \Delta P = (P_i - \frac{na}{V^2})$$

$$P_i V_i = nRT$$

$$\Rightarrow (P_i + \frac{na}{V^2})(V - nb) = nRT$$

- Boyle's Temp: The temperature at which real gases behave like ideal gas is Boyle's temperature

$$(P + \frac{a}{V^2})(V - b) = RT$$

$$\therefore \frac{PV}{RT} = \left(1 + \frac{a}{PV^2}\right)^{-1} \left(1 - \frac{b}{V}\right)^{-1}$$

$$\text{or, } Z = \left(1 - \frac{a}{PV^2}\right) \left(1 + \frac{b}{V}\right)$$

$$\text{or, } Z = 1 + \frac{b}{V} - \frac{a}{PV^2} - \frac{ab}{PV^3}$$

$$\text{or, } 1 = 1 + \frac{b}{V} - \frac{a}{PV^2}$$

$$\therefore \frac{b}{V} = \frac{a}{PV^2}$$

$$\therefore PV = \frac{a}{b}$$

$$\therefore RT = \frac{a}{b}$$

$$\therefore T = \frac{a}{Rb}$$

Boyle's temperature

$$T_B = \frac{a}{Rb}$$

Liquification of Gas:

① Critical Temperature (T_c):

$T > T_c$ No liquification

$T < T_c$ Liquification occurs Liquified.

Temperature above which a gas cannot be ^

② Critical Volume (V_c):

Volume occupied by a real gas at critical temp and Pressure is called Critical volume

③ Critical Pressure (P_c):

$P > P_c$ Liquification occurs

$P < P_c$ Liquification not possible

> Critical Parameters:

At Critical temperature $T = T_c$

$$V = V_c \text{ and } (V - V_c)^3 = 0$$

$$\Rightarrow V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad \text{--- (1)}$$

From 1mol of Van der Waal's equation

$$(P + \frac{a}{V^2})(V - b) = RT$$

$$\text{or } (PV^2 + a)(V - b) = RTV^2$$

$$\text{or } PV^3 - PbV^2 + aV - ab = RTV^2$$

$$\text{or } V^3 - (b + \frac{RT}{P})V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

At $T = T_c$, $P = P_c$ for any V

$$V^3 - (b + \frac{RT_c}{P_c})V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \quad \text{--- (2)}$$

By solving equation (1) and (2) we have

$$V_c = 3b \quad T_c = \frac{8a}{27Rb} \quad P_c = \frac{a}{27b^2}$$

Adiabatic Lapse rate:

For an adiabatic Process we have,

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

$$\Rightarrow \gamma \lambda n T + (1-\gamma) \lambda n P = \lambda n K$$

$$\Rightarrow \gamma \frac{dT}{T} = (\gamma-1) \frac{dP}{P} \quad \text{Also, } P = \rho g h$$

$$\Rightarrow \frac{dP}{P} = \frac{\gamma}{\gamma-1} \frac{dT}{T} \quad dP = -\rho g dh$$

$$\Rightarrow \frac{dP}{P} = \frac{\gamma}{\gamma-1} \frac{dT}{T} \Rightarrow -\frac{\rho g dh}{P} = \frac{\gamma}{\gamma-1} \frac{dT}{T}$$

$$\Rightarrow -\frac{\rho g dh}{RT} = \frac{\gamma}{\gamma-1} \frac{dT}{T}$$

$$\Rightarrow -\frac{Mg dh}{RT} = \frac{\gamma}{\gamma-1} \frac{dT}{T}$$

$$\Rightarrow \frac{dT}{dh} = -\frac{(\gamma-1)}{\gamma} \frac{Mg}{R}$$

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Atmosphere, mainly oxygen and Nitrogen.

$$\text{Avg molecular weight} = \frac{28+32}{2} = 30 \quad \gamma = 1.4$$

$$\text{So, } \frac{dT}{dh} = -\left(\frac{1.4-1}{1.4}\right) \times \frac{30 \times 10^{-3} \times 9.8}{8.314} = 0.01 \text{ m/K}$$

$$\frac{dh}{dT} = 100 \text{ m/K} \Rightarrow \frac{dT}{dh} = \frac{1000}{100} \text{ K/Km} = 10 \text{ K/Km}$$

Thermodynamic Coefficients:

① Isobaric expansion coeff. $\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P$

② Isothermal compressibility $\beta = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T$

③ Bulk modulus. $B = -V \left(\frac{dP}{dV} \right)$

$$B = \gamma_B$$

$$\textcircled{4} \quad \gamma = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V \quad \begin{array}{l} \text{Isochoric pressure Coefficient} \\ \text{Expansion Coefficient} \end{array}$$

> Cyclic Property:

If Z is a function of x and $y \Rightarrow Z = Z(x, y)$

then, $\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$

Here $x = x(y, z)$

or $dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz \quad \text{--- (i)}$

Also $y = y(x, z)$

$$dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \quad \text{--- (ii)}$$

From Equation (i) and (ii) we have

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$\Rightarrow dx = \left(\frac{\partial x}{\partial y} \right)_z \left[\left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \right] + \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$\Rightarrow dx = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x dz + \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$\Rightarrow \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x dz = - \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1}$$

> Mean Free Path:

28.02.2025

There is an elastic collision b/w gas molecules.

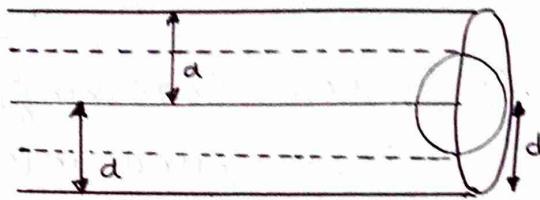
The distance travelled by a gas molecule between two successive collision is free path and taken time to cover the distance is Relaxation time.

$$\lambda_{\text{mean}} = \frac{\sum \pi_i}{N}$$

① classical method:

There is a molecule only which can move but the other remains stationary.

If n be the number density then the number of molecule



$$N = nV \quad \text{Cross Section area} = \pi d^2$$

$$\text{length of the cylinder} = \langle v \rangle \Delta t$$

$$\text{Volume of the cylinder} = \pi d^2 \langle v \rangle \Delta t$$

$$\text{No of Collisions} = n \times V = n \pi d^2 \langle v \rangle \Delta t$$

No of Collisions per second or Collision frequency

$$= \frac{n \pi d^2 \langle v \rangle \Delta t}{\Delta t} = n \pi d^2 \langle v \rangle$$

$$\text{Relaxation time} = \frac{1}{n \pi d^2 \langle v \rangle}$$

$$\lambda = \frac{1}{\pi d^2 n}$$

Avg distance = Avg time \times Avg velocity

$$= \frac{1}{n \pi d^2 \langle v \rangle} \times \langle v \rangle = \frac{1}{\pi d^2 n}$$

② Clausius Method:

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$$

$$n = \frac{N}{V}$$

$$PV = Nk_B T$$

$$\frac{V}{N} = \frac{k_B T}{P}$$

$$\lambda = \frac{V}{\sqrt{2} \pi d^2 N} = \frac{k_B T}{\sqrt{2} \pi d^2 P} \quad \text{At constant volume}$$

$$P \propto T$$

$$T_{\text{mix}} = \frac{n_1 f_1 T_1 + n_2 f_2 T_2}{n_1 f_1 + n_2 f_2}$$

$$\lambda = \text{constant}$$

Thermodynamics

It is a branch of science that deals with thermal energy and its conversion to the other form of energies.

① System: Something that are under our observation and interesting

② Surrounding: Other than the system is called Surrounding.

③ Universe: System + Surrounding = universe.

> State of a System:

Physical quantities that describe the characteristics of a system is called state.

> Equilibrium: with time if the system doesn't changes it state then the condition is Eq_{bm}

> Process:

① Quasi-static Process:

When the process is infinitesimally slow such that each state can be considered as an eq^m state

- Through Boundary only Heat exchange occur diathermic
- Adiabatic wall, Heat exchange doesn't occurs.

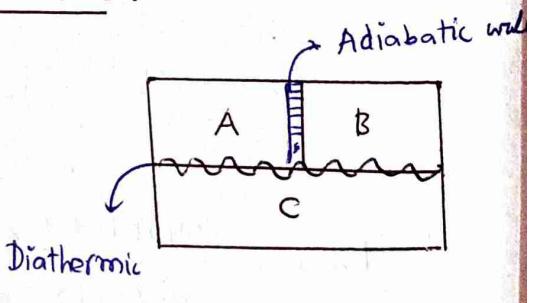
① Zeroth Law of thermodynamics:

if A,C are in therm eq_{bm}

B,C are in therm eq_{L2}

then A,B are also in

thermal eq_{bm}.



After removing of B at $t=t$
also no heat Exchange

Internal Energy

$$IE = KE + PE$$

Internal energy is a state function (Point functions)

For an ideal gas, $U = U(T)$ we can only measure the change in Internal Energy ($\Delta U = U_f - U_i$)

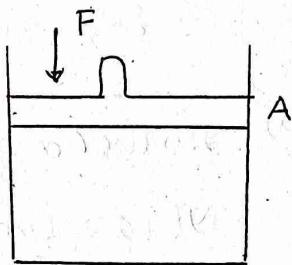
> work done:

work done,

$$dW = Fdx$$

$$\Rightarrow dW = PAdx$$

$$\Rightarrow dW = PdV \Rightarrow W = \int_{V_1}^{V_2} PdV$$



Expansion: work is done by the system

$$dV > 0 \text{ and } dW > 0$$

Compression: work is done on the system

$$dV < 0 \text{ and } dW < 0$$

> work done = Area under PV Curve

It is a path function

> Condition for state Function:

$$A = A(x, y)$$

$$\frac{\partial^2 A}{\partial y \partial x} = \frac{\partial^2 A}{\partial x \partial y}$$

Euler's Condition

Condition for state function

A is exact differential

> Heat Energy: Energy flows due to temperature difference is Heat Energy.

Temperature is the parameter which give the direction of Heat Energy.

- > If ΔQ heat given to a System, $\Delta Q > 0$
- > If $\Delta Q_{\text{not absorb}}$ heat and radiate $\Delta Q < 0$

① First Law of Thermodynamics:

$$\Delta Q = \Delta U + \Delta W \quad w, Q \text{ are Path function}$$

$$dQ = dU + dW$$

(a) Isothermal Process:

$$U(T) = \text{Constant}$$

$$dQ = PdV = dW$$

$$dU = 0, \Delta T = 0$$

$$dQ > 0$$

$$dQ < 0$$

$$dW > 0$$

$$dW < 0$$

Isothermal Expansion

Isothermal Compression

Work done in isothermal Process:

$$w = \int_{V_1}^{V_2} PdV = nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad PV = nRT$$

$$w = nRT \ln\left(\frac{V_2}{V_1}\right)$$

> Isochoric Process:

$$V = \text{Constant}$$

$$dV = 0$$

$$PdV = 0$$

$$dQ > 0, dU > 0$$

$$dQ = dU$$

$$dQ < 0, dU < 0$$

> Adiabatic Process:

$$Q = \text{Constant}$$

$$dQ = 0$$

$$dQ = dU + dW$$

$$dU = -dW$$

$$dV > 0$$

$$dU < 0$$

$$dV < 0 \text{ then } dU > 0$$

$dW > 0$ (work is done by the system)

$dW < 0$ (work is done on the system)

For an Adiabatic Process:

1 mole of ideal gas we have

$$PV = RT$$

$$\text{or } PdV + VdP = RdT$$

$$\text{or } dT = \frac{PdV + VdP}{R} \quad \text{--- (1)}$$

$$dQ = C_V dT + PdV$$

$$\text{or } 0 = C_V \left(\frac{PdV + VdP}{R} \right) + PdV$$

$$\text{or } 0 = \frac{C_V}{R} (PdV + VdP) + PdV$$

$$\text{or } C_V PdV + C_V VdP + RPdV = 0$$

$$\text{or } (C_V + R) PdV + V C_V dP$$

$$\text{or } C_P PdV = -V C_V dP$$

$$\text{or } \int \frac{dV}{V} = -\frac{C_V}{C_P} \int \frac{dP}{P}$$

$$\text{or } PV^\gamma = K$$

Also we have

$$PV = RT \Rightarrow P = \frac{RT}{V}$$

$$\frac{RT}{V} V^\gamma = K \Rightarrow T V^{\gamma-1} = K$$

$$P \cdot \left(\frac{RT}{P}\right)^\gamma = K \Rightarrow P^{1-\gamma} T^\gamma = K$$

Work done in Adiabatic Process:

In adiabatic Process we have, $PV^\gamma = K$

$$P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

$$\text{Work done } w = \int_{V_1}^{V_2} PdV = K \int_{V_1}^{V_2} \frac{1}{V^\gamma} dV = \frac{K}{1-\gamma} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

$$w = \frac{1}{1-\gamma} \left[\frac{K V_2}{V_2^\gamma} - \frac{K V_1}{V_1^\gamma} \right] = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1]$$

$$w = \frac{R}{1-\gamma} [T_2 - T_1]$$

O Cyclic Process:

Initial and final Points are same then the Process will be Cyclic. So $\Delta U = 0$

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

(a) For ideal Gas: $PV = RT$

$$\Rightarrow V = \frac{RT}{P} \quad P = \left(\frac{RT}{V} \right)$$

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

$$C_p - C_v = T \times \frac{R}{P} \times \frac{R}{V} = \frac{R^2 T}{P V} = R \quad C_p - C_v = R$$

(b) For $P(V-b) = RT$: $P(V-b) = RT$

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

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

$$C_p - C_v = T \times \frac{R}{P} \times \frac{R}{V-b} = R$$

(c) For Real Gas:

Van der waal's equation for 1mol of real gas

$$(P + \frac{a}{V^2})(V-b) = RT$$

$$\text{or } P + \frac{a}{V^2} = \frac{RT}{V-b}$$

$$\text{or } P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{or } \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b} \quad \text{--- ①}$$

$$\text{Also, } (P + \frac{a}{V^2}) \left(\frac{\partial V}{\partial T} \right)_P + \left(-\frac{2a}{V^3} \right)(V-b) \left(\frac{\partial V}{\partial T} \right)_V = R$$

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

$$\text{So, } C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

$$\therefore C_p - C_v = T \cdot \frac{R}{(V-b)} \cdot \frac{R}{(P + \frac{a}{V^2}) - (V-b) \frac{2a}{V^3}}$$

$$\text{or } C_p - C_v = \frac{R^2 T}{R.T - \frac{2a}{V}} = \frac{R^2 T}{RT \left[1 - \frac{2a}{RTV} \right]}$$

$$\text{or } C_p - C_v = R \left[1 - \frac{2a}{RTV} \right]$$

$$\text{or } C_p - C_v = R + \frac{2a}{TV}$$

Important Relations:

$$\text{Ratio of specific heat, } \gamma = \frac{C_p}{C_v} \Rightarrow C_p = \gamma C_v$$

Also from Mayer's formula

$$C_p - C_v = R \quad \text{since}$$

$$\text{or } \gamma C_v - C_v = R \quad C_p = \gamma C_v$$

$$\text{or } (\gamma - 1) C_v = R \quad C_p = \frac{\gamma R}{\gamma - 1}$$

$$\text{or } C_v = \frac{R}{(\gamma - 1)}$$

Maxwell's Thermodynamic Relation

$$\text{Helmholtz Free Energy } F = U - TS$$

$$\text{Enthalpy } H = U + PV$$

$$\text{Gibb's Free Energy } G_f = H - TS$$

Including U , they all are state function

only $\oint, \oint w$ are path function

(1) Internal Energy (U)

$$dQ = dU + PdV$$

$$TdS = dU + PdV$$

$$\therefore dU = TdS - PdV$$

If $V = \text{constant}$ $dV = 0$

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

If $S = \text{constant}$ $dS = 0$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S$$

So we have,

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

$$P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial V \partial S}$$

$$-\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V}$$

U is a state function. So

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

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

Maxwell's First thermodynamic Relation

(2) Helmholtz Free Energy (F)

$$F = U - TS$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\text{or } dF = dU - TdS - SdT$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$\therefore dF = TdS - PdV - TdS - SdT$$

$$\therefore dF = -PdV - SdT$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$-\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 F}{\partial V \partial T}$$

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

③ Enthalpy (H):

$$H = U + PV$$

or $dH = dU + PdV + VdP$

$dH = TdS - PdV + PdV + VdP$

or $dH = TdS + VdP$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial^2 H}{\partial S \partial P} \quad \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P}$$

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

④ Gibbs Free Energy (G):

$$G = H - TS$$

$dG = dH - Tds - SdT$

$dG = -PdV - Tds + Vds - Tds - SdT$

a $dG = Vds - SdT$

$$V = \left(\frac{\partial G}{\partial S}\right)_T \quad S = -\left(\frac{\partial G}{\partial T}\right)_S$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial S} \quad \left(\frac{\partial S}{\partial T}\right)_S = -\frac{\partial^2 G}{\partial T \partial S}$$

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

Entropy

Entropy is a measurement of heat that is transferred to a system to make a change in intermolecular interaction, at a particular temperature.

Measurement of disorderliness of a System

$$\text{Entropy, } dS = \frac{dQ}{T} \Rightarrow dQ = TdS$$

From FLOT, we have

$$dQ = dU + PdV \\ \Rightarrow TdS = dU + PdV \Rightarrow dS = \frac{dU + PdV}{T}$$

Change in Entropy:

① dS at const Temperature:

In heat reservoir or Latent heat $\Delta S = \frac{\Delta Q}{T}$, $\Delta S = \frac{mL}{T}$

② dS at change in Temperature:

On heating water Temperature from T_1 to T_2

$$dS = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{mc dT}{T} = mc \ln\left(\frac{T_2}{T_1}\right)$$

$$\boxed{\Delta S = mc \ln\left(\frac{T_2}{T_1}\right)}$$

③ Entropy change for an ideal gas:

$$\text{For. } dS = \frac{dU + PdV}{T}$$

$$dS = \frac{1}{T} (nC_V dT + nR dT)$$

$$\text{Also } dS = \frac{nC_V dT}{T} + \frac{PdV}{T}$$

$$dS = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$\boxed{\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)}$$

Isothermal Process:

$$T_1 = T_2 \quad \Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

Isochoric Process:

$$V_1 = V_2 \quad \Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

Another Way:

$$PV = nRT$$

$$\text{or } PdV + VdP = nRdT$$

$$\text{or } PdV = nRdT - VdP$$

$$dS = \frac{dU + PdV}{T}$$

$$dS = \frac{nC_V dT + nRdT - VdP}{T}$$

$$dS = n(C_V + R) \frac{dT}{T} - \frac{V}{T} dP$$

$$dS = nC_P \frac{dT}{T} - nR \frac{dP}{P}$$

$$\boxed{\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{P_2}{P_1}\right)}$$

Isobaric Process:

$$P_1 = P_2$$

$$\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right)$$

Isothermal Process:

$$T_1 = T_2$$

$$\Delta S = -nR \ln\left(\frac{P_2}{P_1}\right)$$

Case ①: At -10°C , 10 gm ice melt to produce water
At 20°C , 10 gm. Find change in entropy

\Rightarrow Specific heat for water and ice is not same

$$C_{\text{ice}} = 0.5 \text{ cal/gm} \quad C_{\text{water}} = 1 \text{ cal/gm}$$

So, $\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$ is invalid

① -10°C ice $\rightarrow 0^\circ\text{C}$ ice:

$$\Delta S = mC \ln \frac{T_2}{T_1}$$

$$= 10 \times 10^{-3} \times (0.5 \times 4.18 \times 10^3) \times \ln \frac{273}{263}$$

$$= 20.9 \times 0.037 = 0.779 \text{ J/K}$$

Latent heat of
fusion (ice) = 80 cal/g

② $\rightarrow 0^\circ\text{C} \text{ ice} \rightarrow 0^\circ\text{C} \text{ water}$

$$\Delta S = \frac{mL}{T} = \frac{10 \times 10^{-3} \times (80 \times 4.18) \times 10^3}{273} = 12.25 \text{ J/K}$$

③ $0^\circ\text{C} \text{ water} \rightarrow 20^\circ\text{C} \text{ water}$

$$\Delta S = mc \ln\left(\frac{T_2}{T_1}\right) = (10 \times 10^{-3}) \times (1 \times 4.18 \times 10^3) \ln\left(\frac{293}{273}\right) \\ = 2.95 \text{ J/K}$$

Total change in entropy

$$\Delta S = (0.77 + 12.24 + 2.94) = 15.95 \text{ J/K}$$

Case ②

30 gm. 20°C water is converted to 100°C Vapour. Found the change in entropy

① $20^\circ\text{C} \text{ water} \rightarrow 100^\circ\text{C} \text{ water}$

$$\Delta S = mc \ln\left(\frac{T_2}{T_1}\right) \\ = (30 \times 10^{-3}) \times (1 \times 4.18 \times 10^3) \ln\left(\frac{373}{293}\right) \\ = 125.4 \times 0.24 = 30.27 \text{ J/K}$$

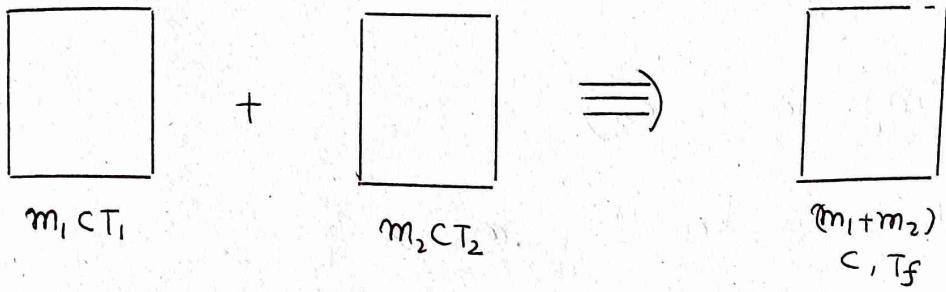
② $100^\circ\text{C} \text{ water} \rightarrow 100^\circ\text{C} \text{ Vapour}$

$$\Delta S = \frac{mL}{T} = \frac{(30 \times 10^{-3}) \times (537 \times 4.18 \times 10^3)}{373} = 180.53 \text{ J/K}$$

Total change in entropy

$$\Delta S = 30.27 + 180.53 = 210.8 \text{ J/K}$$

Entropy of mixing:



Here $T_1 > T_2$ and $T_1 > T_f > T_2$

change in heat energy loss = gain

$$m_1 c (T_1 - T_f) + m_2 c (T_2 - T_f) = 0 \quad \text{So, } \Delta S = 0$$

$$\text{or } m_1 c (T_f - T_1) + m_2 c (T_f - T_2) = 0$$

Mixing Case:

20 gm water at 70°C is mixed with 100 gm of water at 50°C . Find $\Delta S = ?$

$$\Rightarrow m_1 = 20 \text{ gm} = 20 \times 10^{-3} \text{ Kg} \quad m_2 = 100 \times 10^{-3} \text{ Kg}$$

$$T_1 = 70^\circ\text{C} = 343 \text{ K} \quad T_2 = 323 \text{ K}$$

$$C_1 = 1 \text{ Cal/gm} = 4.18 \times 10^3 \text{ J/Kg} \quad C_2 = 4.18 \times 10^3 \text{ J/Kg}$$

$$m_1 c (T_f - T_1) + m_2 c (T_f - T_2) = 0$$

$$\text{or } 20 \times 10^{-3} \times c (T_f - 343) + 100 \times 10^{-3} \times c (T_f - 323) = 0$$

$$\text{or } 20(T_f - 343) = 100 (323 - T_f)$$

$$\text{or } T_f - 343 = 1615 - 5T_f$$

$$\text{or } 6T_f = 1958$$

$$\text{or } T_f = 326.33 \text{ K}$$

So 20 gm water 343K \rightarrow 326.33K

100 gm water 323K \rightarrow 326.33K

change in entropy

$$\begin{aligned}\Delta S &= mc \ln \frac{T_f}{T_i} + mc \ln \frac{T_2}{T_1} \\ &= \left[20 \times 10^{-3} \times 4.18 \times 10^3 \ln \frac{326}{343} \right] + \left[100 \times 10^{-3} \times 4.18 \times 10^3 \ln \frac{326}{323} \right] \\ &= -4.165 + 4.287 = 0.122 \text{ J/K}\end{aligned}$$

> From Previous discussion we have,

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

$$P_1 V_1 = nRT_1$$

$$P_2 V_2 = nRT_2$$

$$\text{or } T_1 = \frac{P_1 V_1}{nR}$$

$$T_2 = \frac{P_2 V_2}{nR}$$

$$\Delta S = nC_p \ln \left(\frac{P_2 V_2}{P_1 V_1} \right) - nR \ln \left(\frac{P_2}{P_1} \right)$$

$$= nC_p \ln \frac{P_2}{P_1} + nC_p \ln \frac{V_2}{V_1} - nR \ln \frac{P_2}{P_1}$$

$$= n(C_p - R) \ln \frac{P_2}{P_1} + nC_p \ln \frac{V_2}{V_1}$$

$$\Delta S = nC_p \ln \frac{V_2}{V_1} + nC_V \ln \frac{P_2}{P_1}$$

In adiabatic Process $\Delta S = C_V \ln \left(\frac{P_2}{P_1} \frac{V_2^\gamma}{V_1^\gamma} \right)$

$$\Delta S = C_V \ln(PV^\gamma) + \text{constant}$$

D) 0.01 Kg of ice at 273K is mixed with 0.1 Kg of water at 300K. Find the change in Entropy

\Rightarrow Phase change + Heat Loss + Heat Gain = 0

$$\text{or } m_1 L + m_1 c_i (T_f - T_i) + m_2 c_w (T_2 - T_f) = 0$$

$$\text{or } (0.01 \times 80 \times 4.18 \times 10^3) + \{ 0.01 \times 4.18 \times 10^3 (273 - T_f) \}$$

$$+ \{ 0.1 \times 4.18 \times 10^3 (300 - T_f) \} = 0 \Rightarrow T_f = 290.29 \text{ K}$$

① 0.01 Kg ice \rightarrow 0.01 Kg water (0°C)

$$\Delta S_1 = \frac{mL}{T} = \frac{0.01 \times 80 \times 4.18 \times 10^3}{273} = 12.249 \text{ J/K}$$

② 273 K water \rightarrow 290.29 K water (0.01 Kg)

$$\Delta S_2 = mc \ln\left(\frac{T_2}{T_1}\right) = 0.01 \times 4.18 \times 10^3 \ln\left(\frac{290}{273}\right) = 2.525 \text{ J/K}$$

③ 300 K water \rightarrow 290.29 K water (0.1 Kg)

$$\Delta S_3 = mc \ln\left(\frac{T_2}{T_1}\right) = 0.1 \times 4.18 \times 10^3 \ln\left(\frac{290}{300}\right) = -9.8 \text{ J/K}$$

Change in entropy $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$= 12.249 + 2.525 - 9.8 = 4.95 \text{ J/K}$$

④ A Solid at temperature T_1 is brought in contact with a heat reservoir at temperature $T_2 (> T_1)$. In due course of time, the system attains thermal equl. The change in entropy of the universe

\Rightarrow Entropy change of solid.

$$\Delta S_s = mc_p \int \frac{dT}{T} = mc_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\text{of the reservoir, } \Delta S_r = - \frac{mc_p (T_2 - T_1)}{T_2}$$

Entropy change of the universe,

$$\Delta S_u = mc_p \ln\left(\frac{T_2}{T_1}\right) - \frac{mc_p (T_2 - T_1)}{T_2}$$

Heat Engine:

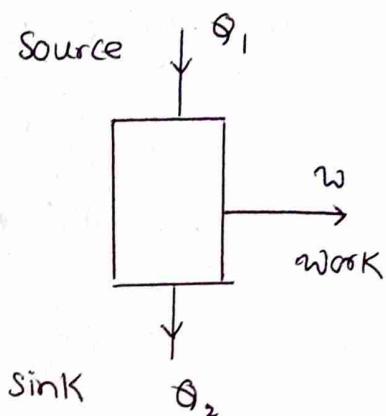
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A machine that converts heat energy into work (Mechanical work).

Efficiency:

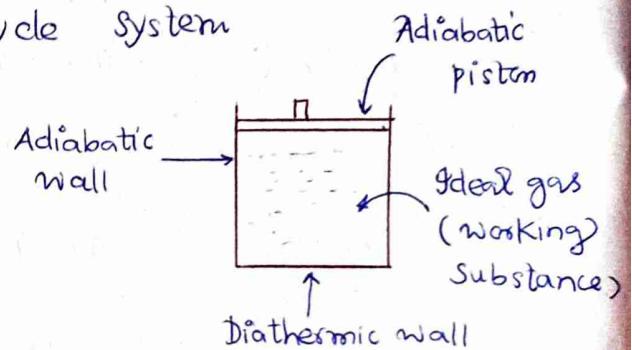
$$w = Q_1 - Q_2 \quad \text{Also, } \eta = 1 - \frac{T_2}{T_1}$$

$$\begin{aligned} \eta &= \frac{w}{Q_1}, \quad 0 < \eta < 1 \quad \frac{T_2}{T_1} = \frac{Q_2}{Q_1} \\ &= \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \end{aligned}$$

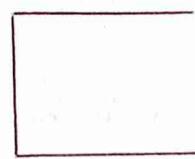


① Carnot Engine (Theoretical Engine)

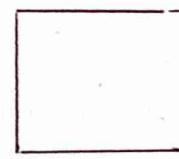
work on Carnot cycle system



Heat reservoir
: Source (T_1)



Insulated
Mount



Sink (T_2)
where, $T_1 > T_2$

Infinite heat capacity

- ① System put on source (T_1) for infinite time, so the gas will expand at constant temperature

Isothermal Expansion: $\Delta Q = \Delta U + \overset{\circ}{\Delta W}$

$A \rightarrow B$

$$\Delta Q = \Delta W = nRT_1 \ln\left(\frac{V_2}{V_1}\right) - ①$$

② Now the System put on the insulated mount so the whole System became insulated. The System is not exchange any heat so,

Adiabatic Process: $\Delta Q = 0$

Expansion Occurs: $B \rightarrow C$

$$w = \frac{nR}{1-\gamma} (T_2 - T_1) \quad \text{Expansion will occur till the temperature became } T_2$$

Adiabatic Expansion \rightarrow decrease in the internal Energy so gas became colder ($T_2 < T_1$)

Slope | Adiabatic $>$ Slope | Isothermal

③ when it put in Sink (T_2) it is isothermal Process and compression will occur

Isothermal Compression

$$\text{work done } w = nRT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$C \rightarrow D$

$$dV < 0 \text{ so } \Delta w < 0 \text{ so } \Delta Q < 0$$

Heat energy became rejected

④ Then it put on insulated mount

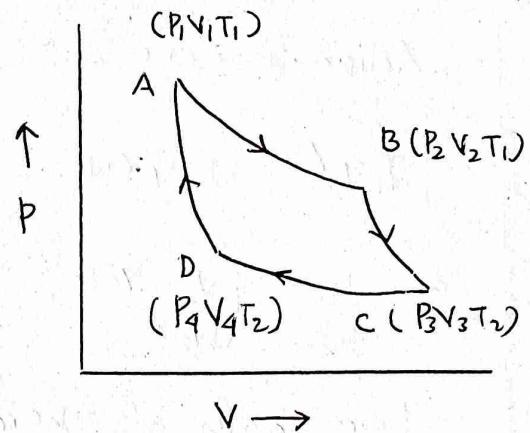
Now here $\Delta w < 0$ $\Delta U > 0$ Temperature increase
 $\Delta Q = 0$ Adiabatic Compression

$$w = \frac{nR}{1-\gamma} [T_1 - T_2] \quad D \rightarrow A$$

Total work done in the process

$$w = nRT_1 \ln\left(\frac{V_2}{V_1}\right) + \frac{nR}{1-\gamma} (T_2 - T_1) + nRT_2 \ln\left(\frac{V_4}{V_3}\right) + \frac{nR}{1-\gamma} (T_1 - T_2)$$

$$w = nRT_1 \ln\left(\frac{V_2}{V_1}\right) + nRT_2 \ln\left(\frac{V_4}{V_3}\right) \quad \text{--- ①}$$



Adiabatic Process B → C

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{or } \frac{T_1}{T_2} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

$$\text{From both of them, } \frac{V_3}{V_2} = \frac{V_q}{V_1} \Rightarrow \frac{V_q}{V_3} = \frac{V_1}{V_2} \quad \text{--- (6)}$$

From Equation ① and ② we have

$$W = nRT_1 \ln \frac{V_2}{V_1} + nRT_2 \ln \frac{V_1}{V_2}$$

$$W = nRT_1 \ln \frac{V_2}{V_1} - nRT_2 \ln \frac{V_2}{V_1}$$

$$W = nR \ln \left(\frac{V_2}{V_1} \right) [T_1 - T_2] \quad \text{--- (1)}$$

Extracted heat, $Q_1 = nRT_1 \ln \frac{V_2}{V_1}$

$$\text{Efficiency, } \eta = \frac{W}{Q_1} = \frac{nR \ln \left(\frac{V_2}{V_1} \right) [T_1 - T_2]}{nRT_1 \ln \left(\frac{V_2}{V_1} \right)} = 1 - \frac{T_2}{T_1}$$

$$\eta = (1 - T_2/T_1)$$

Adiabatic Expansion Ratio (γ)

Ratio of volume where gas expands

$$\text{adiabatically, } \gamma = \frac{V_3}{V_2}$$

$$T_2 V_3^{\gamma-1} = T_1 V_2^{\gamma-1} \Rightarrow \left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_1}{T_2}$$

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

$$T_2 < T_1$$

Absolute temperature

$$\text{Efficiency, } \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{1}{\gamma^{\gamma-1}}$$

$$\boxed{\eta = 1 - \left(\frac{1}{\gamma}\right)^{\gamma-1}}$$

$$dQ = TdS$$

$$dS < 0$$

$$dQ < 0$$

System will reject heat Energy

$$dS > 0$$

$$dW > 0$$

System will gain heat Energy

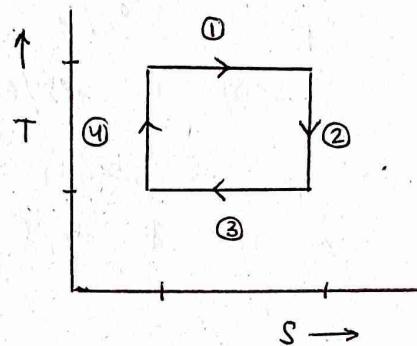
On T-S diagram:

$$\textcircled{1} \quad dQ > 0, \quad dS > 0, \quad T = \text{constant}$$

$$\textcircled{2} \quad dQ = 0, \quad dS = 0, \quad T = \text{decrease}$$

$$\textcircled{3} \quad dQ < 0, \quad dS < 0, \quad T = \text{constant}$$

$$\textcircled{4} \quad dQ = 0, \quad dS = 0, \quad T = \text{increase}$$



\textcircled{1} what will be Efficiency

=>

Heat absorb

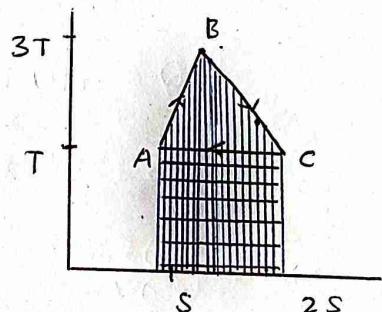
$$Q_1 = ST + \frac{1}{2} \times S \times 2T = 2ST$$

Heat rejected

$$Q_2 = ST$$

work done, $w = Q_1 - Q_2$

$$w = 2ST - ST = ST$$



$$\text{Efficiency, } \eta = \frac{w}{Q_1} = \frac{ST}{2ST} = \frac{1}{2}$$

Refrigerator:

Reverse of the Carnot Cycle.

- * In refrigerator working substance remove the heat energy from the object kept inside. So some external work has to be done

This work done is provided by Electricity.

$$Q_2 + w = Q_1 \Rightarrow \text{Rejected in environment}$$

(Back of freeze, compression)

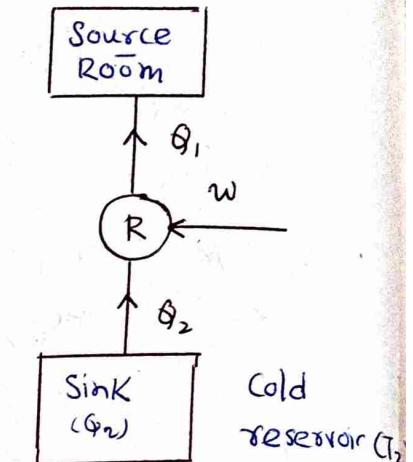
Coefficient of Performance

$$COP = \frac{\text{Rejected Heat}}{\text{Work done on it}}$$

$$COP = K = \frac{Q_2}{Q_1 - Q_2}$$

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

$$K = \frac{T_2/T_1}{1 - T_2/T_1} = \frac{1-\eta}{\eta} \Rightarrow$$



$$K = \frac{1}{\eta} - 1$$

11.03.2024

From FLOT and SLOT we have,

$$dQ = dU + PdV$$

$$\sim TdS = dU + PdV$$

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

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

Ideal Gas:

$$PV = RT$$

$$(P + \frac{a}{V^2})(V - b) = RT$$

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

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

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

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

$$\left(\frac{\partial U}{\partial V} \right)_T = P - P = 0$$

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

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{a}{V^2}$$

Real Gas:

① T-S Relation of 1st Kind:

Let us Consider, $S = S(T, V)$

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

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

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

$$TdS = C_V dT + P_T \cdot \frac{1}{P} \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\therefore TdS = C_V dT + P_T V dV$$

② T-ds Relation of 2nd Kind:

Here we have $S = S(T, P)$

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

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

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

$$TdS = C_P dT - V_T \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$TdS = C_P dT - V_T \alpha dP$$

Relation between C_P & C_V

From Equation ① and ② we have

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

So,

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

Clausius Clapeyron Equation:

From Maxwell's thermodynamic relation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \text{or} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{mL}{T(V_2 - V_1)}$$

$$\text{or } T \left(\frac{\partial P}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial V}\right)_T \quad \text{or} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{T\left(\frac{V_2}{m} - \frac{V_1}{m}\right)}$$

$$\text{or} \quad T \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\Delta S}{\Delta V}\right)_T \quad \text{or} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{T(v_2 - v_1)}$$

$$\text{or} \quad T \left(\frac{\partial P}{\partial T}\right)_V = \frac{mL}{(V_2 - V_1)} \quad (v = \frac{V}{M} = \text{specific volume})$$

So we have,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{T(v_2 - v_1)}$$

Melting of ice:

$$v_{\text{ice}} > v_w$$

$$v_{w_1} > v_2$$

Since $v_1 > v_2$. So $\left(\frac{\partial P}{\partial T}\right)_V$ is Negative.

with Pressure melting point decreases.

Vaporization/Boiling: $v_2 \rightarrow$ volume of vapour

$$v_2 > v_1 \quad v_1 \rightarrow \text{volume of water}$$

So $\left(\frac{\partial P}{\partial T}\right)_V$ is positive

with Pressure boiling point increase

If Pressure decrease, boiling point also decrease.

Phase Transition.

① First order Phase Transition:

Phase transition where latent heat is involved
is called first order phase transition

Melting, Boiling) are Examples

② Second order Phase Transition:

Phase transition where latent heat is ^{not} involved.

At λ -point temperature.

Conversion of Paramagnetic to diamagnetic.
and Super Conductivity

Young's Equation

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{T(V_{\text{vap}} - V_{\text{liq}})}$$

$$\text{or } \frac{dP}{dT} = \frac{L}{TV_{\text{vap}}} \quad (\text{Since, } V_{\text{vap}} \gg V_{\text{liq}})$$

$$\text{or } \frac{dP}{dT} = \frac{LP}{TRT} \quad \begin{array}{l} PV = RT \quad \text{Ideal} \\ V = \frac{RT}{P} \quad \text{gas} \end{array}$$

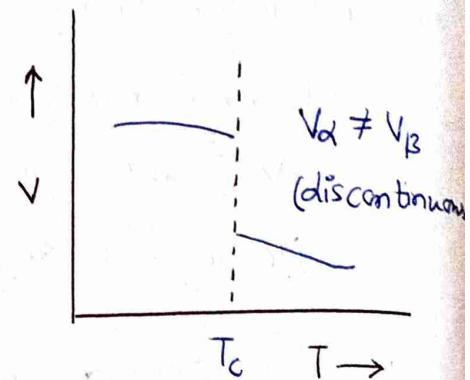
$$\therefore \int \frac{dP}{P} = \frac{L}{R} \int \frac{dT}{T^2}$$

$$\boxed{\ln P = -\frac{L}{R} \frac{1}{T} + C}$$

Relation between pressure
and temperature

Ehrenfest Classification of Phase Transition

① First Order:



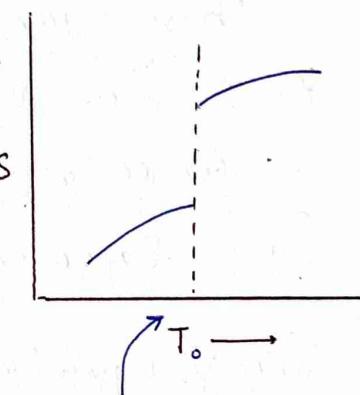
At transition point.
temperature doesn't change
but entropy in form of
latent heat. and Here
Pressure remain Constant

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = VdP + TdS - TdS - SdT \Rightarrow$$

$$dG = VdP - SdT$$



$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

Phase Transition of order n: (α, β are two phases)

$$\left(\frac{\partial^m G_\alpha}{\partial P^m} \right)_T = \left(\frac{\partial^m G_\beta}{\partial P^m} \right)_T$$

Here

$$\left(\frac{\partial^m G_\alpha}{\partial T^m} \right)_P = \left(\frac{\partial^m G_\beta}{\partial T^m} \right)_P$$

$$m = 0, 1, 2, 3, \dots (n-1)$$

① First order:

when $m=0$ and $n=1$

$$\left(\frac{\partial^0 G_\alpha}{\partial P^0} \right)_T = \left(\frac{\partial^0 G_\beta}{\partial P^0} \right)_T \Rightarrow \boxed{G_\alpha = G_\beta}$$

Gibbs free energy is continuous

$$\left(\frac{\partial^m G_\alpha}{\partial P^m} \right)_T \neq \left(\frac{\partial^m G_\beta}{\partial P^m} \right)_T$$

$$\left(\frac{\partial^m G_\alpha}{\partial T^m} \right)_P \neq \left(\frac{\partial^m G_\beta}{\partial T^m} \right)_P$$

$$m > n$$

$$\underline{n=1, m=1: \quad (m=n)}$$

$$\left(\frac{\partial G_\alpha}{\partial P} \right)_T \neq \left(\frac{\partial G_\beta}{\partial P} \right)_T \quad \left(\frac{\partial G_\alpha}{\partial T} \right)_P \neq \left(\frac{\partial G_\beta}{\partial T} \right)_P$$

$$\Rightarrow V_\alpha \neq V_\beta \quad \Rightarrow S_\alpha \neq S_\beta$$

Entropy and volume both are discontinuous in first order phase transition.

② Second order

$$\underline{n=2, m=0: \quad G_\alpha = G_\beta}$$

Gibbs free energy is Continuous

$$\underline{n=2, m=1: \quad \left(\frac{\partial G_\alpha}{\partial T} \right)_P = \left(\frac{\partial G_\beta}{\partial T} \right)_P \Rightarrow S_\alpha = S_\beta}$$

$$\left(\frac{\partial G_\alpha}{\partial P} \right)_T = \left(\frac{\partial G_\beta}{\partial P} \right)_T \Rightarrow V_\alpha = V_\beta$$

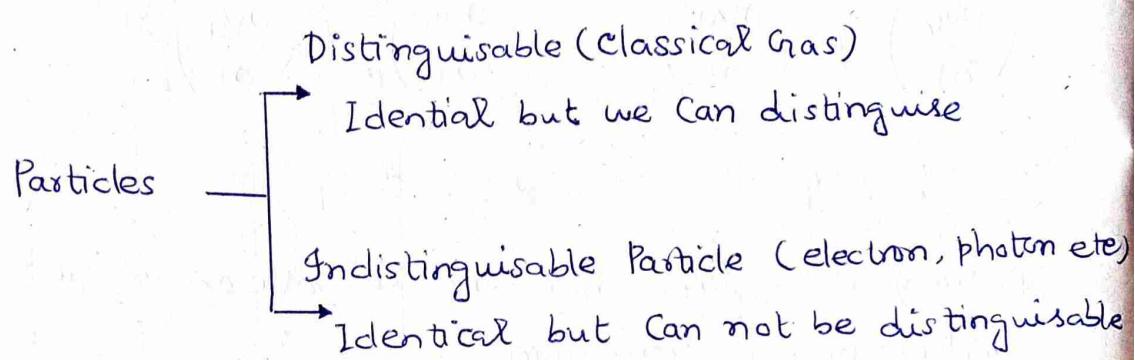
S, V both are continuous at Second order.

$$\underline{n=2, m=2: \quad C_P = T \left(\frac{\partial^2 G_\alpha}{\partial T^2} \right)_P \neq T \left(\frac{\partial^2 G_\beta}{\partial T^2} \right)_P}$$

both C_P, α, β is discontinuous. $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$

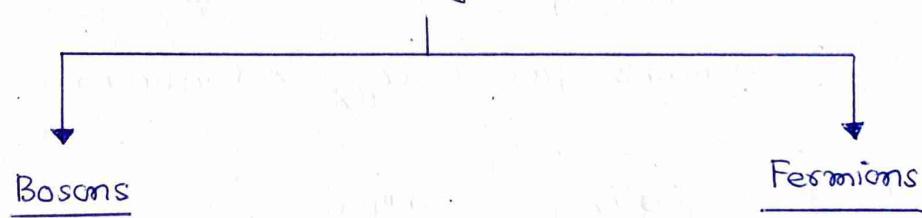
- > Thermodynamics deals with Macrostates. It is mainly experimental Base.
- > KTG deals with Microstate at molecular level

velocity → momentum → force → Pressure
 ← Microstate → Macrostate →
- > Statistical mechanics, we goes Micro to Macrostate.
- > In KTG, every molecule is tracked but in stat mechanics we see every behaviour (Average).
- > So, KTG is more than statistical mechanics (Tough)



Microstate:

Quantum Particles
(Indistinguishable)

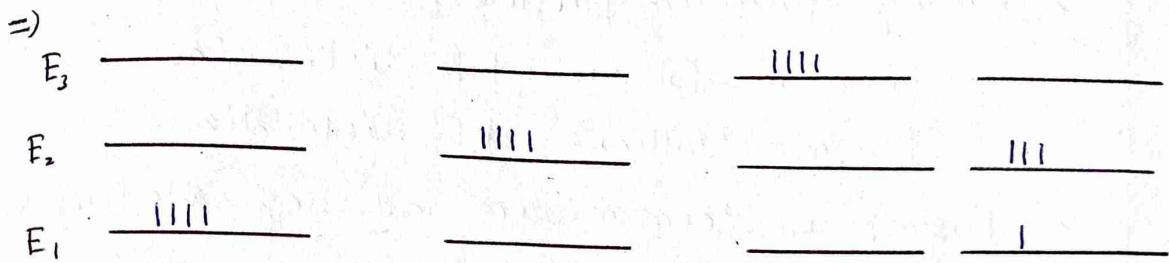


- Having integral spin
($0, \pm 1, \pm 2, \pm 3 \dots$)
- Brotherhood.
- Having odd half integral spin
($\pm \frac{1}{2}, \pm \frac{5}{2}, \pm \frac{7}{2} \dots$)
- Having no brotherhood.

Pauli Exclusion Principle: Two fermions can't stay in a same state of energy level

Statistical Mechanics

① There are 4 Bosons and 3 Energy state.



Like that there are many state

E_1	E_2	E_3	
4	0	0	
0	4	0	
0	0	4	
3	1	0	
3	0	1	
1	3	0	
1	0	3	
0	1	3	
2	2	0	
2	0	2	
0	2	2	
2	1	1	
1	2	1	
1	1	2	

The different states are microstate.

So number of microstate is 15

Fermions

g is no of energy state

n is no of particle

$g \geq n$

② There are 3 energy state, 3 particle

so for fermions there are 3 fermions Maximum

\Rightarrow

1		
	1	
		1

way of distribution is 1
No of microstate = 1

③ There are 2 Fermions 3 energy state

\Rightarrow

1	1	1
1	1	1

No of microstate is 3

> classical gas particle are distinguishable and they follows Maxwell Boltzman distribution

> Among quantum particles,

Fermion follows FD distribution

Bosons follows BE distribution

> Bosons are Fermions are indistinguishable Particle

① Consider a system of 2 particle having 3 quantum states $0, \epsilon, 2\epsilon$. Find number of microstate

⇒ (i) classical Particle: They are distinguishable A,B

Available energy state,

0	ϵ	2ϵ	Total Energy	Microstate
AB	0	0	0	1
0	AB	0		
A	0	B	2ϵ	3
B	0	A		
0	A	B	3ϵ	2
0	B	A		
B	A	0	ϵ	2
A	B	0		
0	0	AB	4ϵ	1

(ii) Bosons:

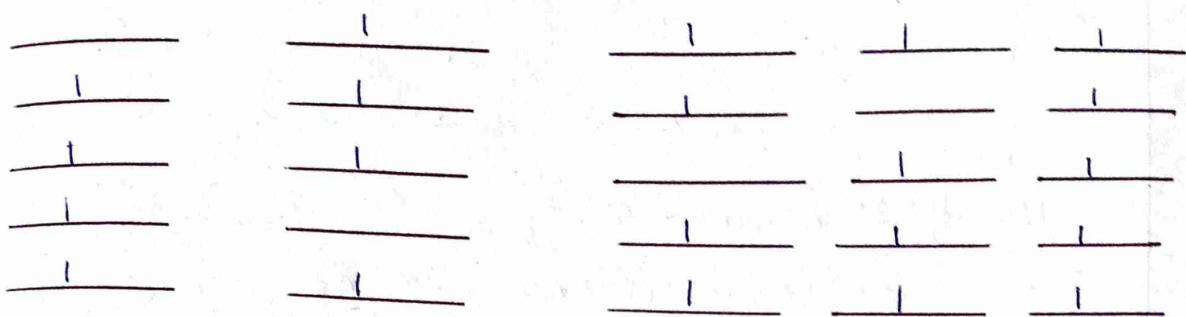
0	ϵ	2ϵ	E	Microstate
11	0	0	0	1
0	11	0		
1	0	1	2ϵ	2
1	1	0	ϵ	1
0	1	1	3ϵ	1
0	0	11	4ϵ	1

(iii) Fermions

0	ϵ	2ϵ	E	Microstate
1	1	0	ϵ	1
1	0	1	2ϵ	1
0	1	1	3ϵ	1

Fermions

- ① where, we have 4 fermions and 5 energy state

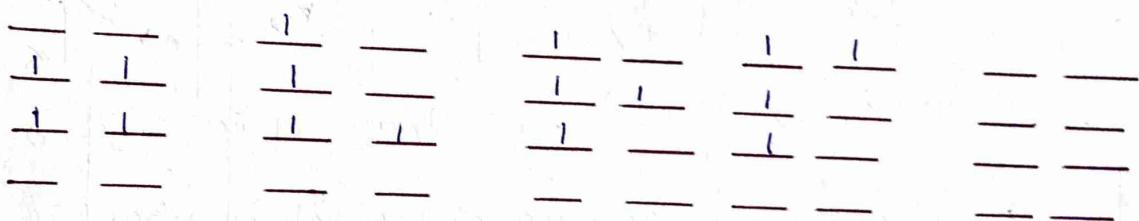


$$\text{No of microstate} = 5$$

$$\text{Entropy, } S = K \ln \Omega = K \ln 5$$

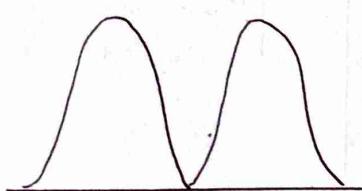
This is applicable when spin is not mentioned.

- ② 4 Fermions of Spin $\frac{1}{2}$ have 3 energy state $\epsilon_{Cu} = 15$
- \Rightarrow Degeneracy. $g = 2s+1 = 2$



- ③ There are 6 Boson with spin 2 and 3 energy level.
Find the number of microstate

$\Rightarrow g = 2s+1$ will not be applicable here
because Boson doesn't follow Pauli exclusion principle. So they all remain same in a single state. So number of microstate is 1.



Distinguishable Ψ



Indistinguishable Ψ

Three electron and 2 energy state are given.

$$\Rightarrow \text{Degeneracy } S = \frac{1}{2} \quad g = 2S+1 = 2$$

$$\begin{array}{c} \underline{\underline{1}} \\ \underline{\underline{1}} \end{array} \quad \begin{array}{c} \underline{\underline{1}} \\ \underline{\underline{1}} \end{array} \quad \begin{array}{cc} \underline{\underline{1}} & \underline{\underline{1}} \\ \underline{\underline{1}} & \underline{\underline{1}} \end{array} \quad \begin{array}{cc} \underline{\underline{1}} & \underline{\underline{1}} \\ \underline{\underline{1}} & \underline{\underline{1}} \end{array}$$

No of Microstate = 4

$$\text{Entropy } S = k \ln 4 = 2k \ln 2$$

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① Phase Space:

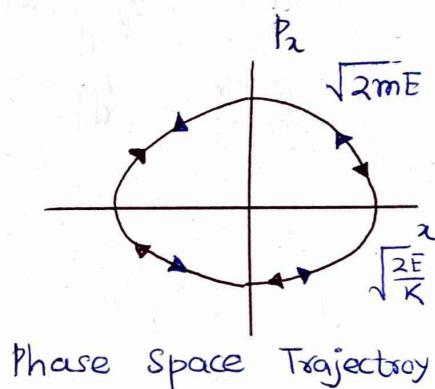
Energy must be constant

For Simple Harmonic Oscillator,

$$\frac{p^2}{2m} + \frac{1}{2}Kx^2 = E$$

$$\therefore \frac{p_x^2}{(\sqrt{2mE})^2} + \frac{x^2}{(\sqrt{\frac{2E}{K}})^2} = 1$$

(Equation of Ellipse.)



Phase Space Trajectory

If energy increases, the ellipse will be bigger.

Two phase space trajectory never intersect each other

since E is constant so

if $p_x \uparrow$ and $x \downarrow$; $p_x \downarrow$ $x \uparrow$

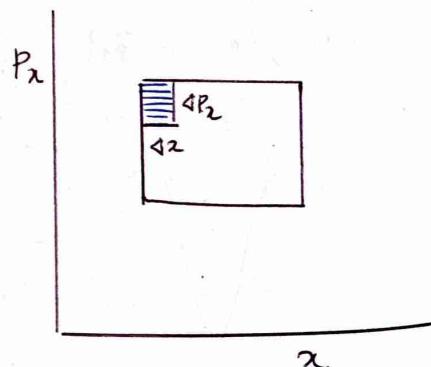
so from here we get the direction is both

> Heisenberg uncertainty

$$\Delta x \Delta p \sim h$$

the minimum area

is $h (10)$

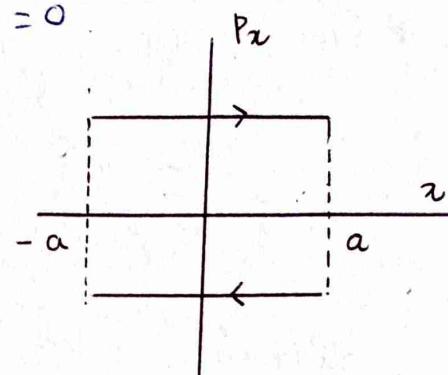


① Particle in a Box:

Here Potential inside the box is zero as it is freely movable so $V(x) = 0$

$$E = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

E is constant and not depends on x .

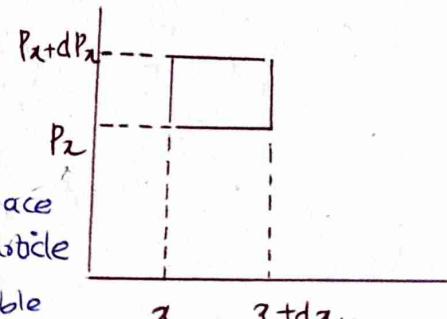


By using phase Space Trajectory, if we know the momentum and Position of an object at any time t , then we can locate the exact position and the momentum of the Particle at any later time.

> Density of state:

No of phase Space

$$\text{point} = \frac{dx dp_x}{h} \Rightarrow \text{Minimum space to put a particle}$$



$$\text{DOS}_{1D} = \frac{dx dp_x}{h} \Rightarrow \text{No of available energy state}$$

$$\text{DOS}_{2D} = \frac{dx dy dp_x dp_y}{h^2}$$

$$\text{DOS}_{3D} = \frac{dx dy dz dp_x dp_y dp_z}{h^3}$$

In 1-D: Density of state.

$$g(P) dP = \frac{dx dp}{h} = \frac{L dP}{h}$$

$$g(E) = \frac{d\Omega}{dE}$$

No of available energy state in the range P to $(P + dP)$

$$\text{In 2-D: } g(P) dP = \frac{dx dy dp_x dp_y}{h^2} = \frac{A \cdot 2\pi P dP}{h^2}$$

$$\text{In 3-D: } g(P) dP = \frac{dx dy dz dp_x dp_y dp_z}{h^3} = \frac{V \cdot 4\pi P^2 dP}{h^3}$$

> No. of available energy state in the range
 E to $E+dE$ $g(E)dE$

• Free Particle:

$$E = \frac{p^2}{2m}$$

$$\text{or } 2mdE = 2pdP$$

$$\therefore dP = \sqrt{\frac{m}{2}} E^{-\frac{1}{2}} dE$$

$$g(E)dE = \frac{LdP}{h}$$

$$g(E)dE = \frac{L}{h} \sqrt{\frac{m}{2}} E^{-\frac{1}{2}} dE \quad (\text{One dimension})$$

2D:

$$g(E)dE = \frac{A}{h^2} \cdot 2\pi PdP$$

$$g(E)dE = \frac{A}{h^2} 2\pi \sqrt{2mE} \sqrt{\frac{m}{2}} E^{-\frac{1}{2}} dE$$

$$= \frac{A}{h^2} 2\pi \sqrt{\frac{2mE \cdot m}{2E}} dE$$

$$= \frac{A}{h^2} 2\pi m dE$$

NOTE: If $E \propto P^s$ then $g(E) \propto E^{d/s-1}$
 (Here d is dimension)

Confirmation

$$\text{For free Particle } E = \frac{p^2}{2m} \Rightarrow E \propto P^2$$

$$\text{So. } s=2$$

$$g(E) \propto E^{d/s-1}$$

$$g(E) \propto E^{\frac{1}{2}-1} \propto E^{-\frac{1}{2}} \quad (\text{ID})$$

2D

$$g(E) \propto E^{d/s-1}$$

$$d=2 \\ s=2$$

$$g(E) \propto E^0$$

- Density of state for Photon Gas:

In three dimension

$$E = PC$$

$$dP = \frac{1}{c} dE$$

$$g(P) dP = \frac{V}{h^3} 4\pi P^2 dP \Rightarrow \frac{V 4\pi}{h^3} \frac{E^2}{c^2} \frac{dE}{c} = g(E) dE$$

$$g(E) dE \propto E^2 dE$$

So here, $E dP$ and $s=1$, $d=3$

$$g(E) dE \propto E^{d/s-1} dE \propto E^{3-1} \propto E^2 dE$$

(Verified)

- Density of state for Simple Harmonic Oscillator

Energy of the system

$$E = \frac{Px^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$\frac{Px^2}{(\sqrt{2mE})^2} + \frac{x^2}{(\frac{\sqrt{2E}}{m\omega})^2} = 1$$

$$\text{Area} = \pi \sqrt{2mE} \sqrt{\frac{2E}{m\omega^2}} = \frac{2E\pi}{\omega}$$

$$\text{Density of state } g(E) dE = \frac{2\pi}{\omega h} dE$$

$$\text{NOTE: } \Omega = \frac{\int d^3x \int d^3p}{h^3}$$

No of accessible state per unit energy is called density of state. So $g(E) = \frac{d\Omega}{dE}$

Concept of Partition Function

17.03.24

Mathematically, Partition Function is

$$\text{defined as, } Z = \sum e^{-\beta E_i}$$

> Let there are two energy state but types of the particle is not mentioned. then $Z = e^{-\beta E_1} + e^{-\beta E_2}$

> For three energy state $\epsilon, 0, -\epsilon$ then Partition function. $Z = e^{-\beta \epsilon} + e^{-\beta \times 0} + e^{\beta \epsilon} = 1 + e^{\beta \epsilon} + e^{-\beta \epsilon}$

> If degeneracy is present then,

$$\begin{array}{c} \text{--- --- ---} \\ \text{--- --- ---} \end{array} \epsilon \quad \text{Partition Function}$$

$$\begin{array}{c} \text{--- --- ---} \\ \text{--- --- ---} \end{array} 0 \quad Z = e^{\beta \epsilon} + e^{-\beta \times 0} + e^{-\beta \times 0} + 3e^{-\beta \epsilon}$$

$$\begin{array}{c} \text{--- --- ---} \\ \text{--- --- ---} \end{array} -\epsilon \quad Z = e^{\beta \epsilon} + 2 + 3e^{-\beta \epsilon}$$

> If state have degeneracy g_i , then the partition function will be

$$Z = \sum g_i e^{-\beta \epsilon_i} \quad (\beta = \frac{1}{k_B T})$$

> One dimensional Simple harmonic Oscillator

$$E_n = (n + \frac{1}{2}) \hbar \omega. \text{ Energy states are}$$

$$\frac{\hbar \omega}{2}, \frac{3}{2} \hbar \omega, \frac{5}{2} \hbar \omega, \dots, \frac{7}{2} \hbar \omega, \frac{9}{2} \hbar \omega, \dots \text{ up to}$$

$$\text{Partition function} = e^{-\frac{\beta \hbar \omega}{2}} + e^{-\beta \times \frac{3}{2} \hbar \omega} + e^{-\beta \times \frac{5}{2} \hbar \omega} + e^{-\beta \times \frac{7}{2} \hbar \omega} + \dots$$

$$a = e^{-\frac{\beta \hbar \omega}{2}} \quad r = e^{-\beta \hbar \omega} \quad (\text{Common ratio})$$

$$Z = \frac{a}{1-r} = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}} = \frac{e^{-\beta \hbar \omega / 2}}{e^{-\frac{\beta \hbar \omega}{2}} [e^{\frac{\beta \hbar \omega}{2}} - e^{-\frac{\beta \hbar \omega}{2}}]}$$

$$Z = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}} = \frac{1}{2} \operatorname{Cosech} \frac{\beta \hbar \omega}{2}$$

- ① There are 2 fermions having energy states $0, \epsilon, -\epsilon, 2\epsilon$. If all of them are nondegenerate.

\Rightarrow

$-\epsilon$	0	ϵ	2ϵ	E
1	1	0	0	$-\epsilon$
1	0	1	0	0
1	0	0	1	ϵ
0	1	1	0	ϵ
0	1	0	1	2ϵ
0	0	1	1	3ϵ

Partition Function

$$Z = e^{\beta E} + 1 + e^{-\beta \times 2\epsilon} + 2e^{-\beta \epsilon}$$

$$+ e^{-\beta \times 3\epsilon}$$

$$Z = 1 + e^{\beta \epsilon} + 2e^{-\beta \epsilon} + e^{-2\beta \epsilon} + e^{-3\beta \epsilon}$$

②

3 Energy state $(0, -\epsilon, \epsilon)$ 2 Bosons find Z

\Rightarrow

$-\epsilon$	0	ϵ	E
2	0	0	-2ϵ
0	2	0	0
0	0	2	2ϵ
1	1	0	$-\epsilon$
1	0	1	0
0	1	1	ϵ

Partition Function

$$Z = e^{-\beta(-2\epsilon)} + e^{-\beta(-\epsilon)}$$

$$+ 2e^{-\beta \times 0} + e^{-\beta \epsilon} + e^{-\beta \times 2\epsilon}$$

$$= 2 \left(\frac{e^{2\beta\epsilon} + e^{-2\beta\epsilon}}{2} \right) + 2 + 2 \left(\frac{e^{-\beta\epsilon} + e^{\beta\epsilon}}{2} \right)$$

$$= 2 \cosh 2\beta\epsilon + 2 + 2 \cosh \beta\epsilon$$

> Average of average of a function is average ($\bar{\bar{x}} = \bar{x}$)

- $\langle x+x^2 \rangle = \langle x \rangle + \langle x^2 \rangle$

- $\langle x - \langle x \rangle \rangle = \langle x \rangle - \langle \langle x \rangle \rangle = \langle x \rangle - \langle x \rangle = 0$

- $\overline{(x - \bar{x})^2} = \overline{x^2 + (\bar{x})^2 - 2x\bar{x}} = \bar{x}^2 + (\bar{x})^2 - 2\bar{x}\bar{x}$

$$\sigma^2 = \bar{x}^2 + (\bar{x})^2 - 2(\bar{x})^2 = \bar{x}^2 - (\bar{x})^2$$

Standard deviation

$$\sigma = \sqrt{\bar{x}^2 - (\bar{x})^2}$$

- Average Energy = $\frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \langle E \rangle$

- E_3 _____
- E_2 _____
- E_1 _____

Average Energy

$$\langle E \rangle = \frac{E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2} + E_3 e^{-\beta E_3}}{e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}}$$

(Internal Energy of the system)

Average Energy

- $Z = \sum e^{-\beta E_i}$

$$\langle E \rangle = - \frac{\partial}{\partial \beta} (\ln Z)$$

- or $\ln Z = \ln \left[\sum e^{-\beta E_i} \right]$

- or $- \frac{\partial}{\partial \beta} (\ln Z) = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \langle E \rangle$

$$\beta = \frac{1}{K_B T}$$

- $\langle E \rangle = - \frac{\partial}{\partial \beta} (\ln Z) = - \frac{\partial}{\partial \beta} \left(\frac{\partial T}{\partial \beta} \right) \ln Z$

$$\langle E \rangle = K_B T^2 \frac{\partial}{\partial T} (\ln Z)$$

$$\beta = \frac{1}{K_B T}$$

$$\frac{\partial \beta}{\partial T} = - \frac{1}{K_B T^2}$$

Stirly Approximation

$$\ln n! = n \ln n - n$$

$$\ln n! = \ln (1 \cdot 2 \cdot 3 \cdot 4 \cdots n)$$

$$= \ln 1 + \ln 2 + \ln 3 + \ln 4 \cdots \ln n$$

$$= \sum_{i=1}^n \ln i = \int \ln n dn = n \ln n - n$$

Fraction of Particles:

For three energy state E_1, E_2, E_3 the partition function will be

$$Z = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}$$

Fraction of Particle in the energy state E_2 is given

$$\text{by } p(E_2) = \frac{e^{-\beta E_2}}{Z} = \frac{e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}}$$

> Partition Function for a Continuous System.

$$Z = \frac{1}{h^3} \int e^{-\beta E} d^3x d^3p$$

① An one-dimensional system having $V(x) = \alpha|x|$

Hamiltonian of the System, $V(x) = \alpha|x|$

Partition function. $Z = \frac{1}{h} \int e^{-\beta E} dx dp$

$$Z = \frac{1}{h} \int e^{-\beta \left(\frac{p^2}{2m} + \alpha|x| \right)} dx dp$$

$$Z = \frac{1}{h} \left[\int_{-\infty}^{+\infty} e^{-\frac{\beta p^2}{2m}} dp \cdot 2 \int_0^{\infty} e^{-\alpha \beta x} dx \right]$$

$$\int_{-a}^a f(x) dx = 2 \int_0^a f(x) dx \Rightarrow \text{Even function, Symmetric limits}$$

$$Z = \frac{2}{h} \sqrt{\frac{2\pi k}{\beta}} \frac{1}{\alpha^\beta}$$

* Grand Canonical partition function

$$Z_G = \exp \left[e^{\frac{\mu}{kT}} Z_N \right]$$

② One dimensional system having, $V(x) = \frac{1}{2}kx^2$

Total energy of the system,

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

$$\text{Partition function } Z = \frac{1}{h} \int e^{-\beta H} dx dp$$

$$Z = \frac{1}{h} \int e^{-\beta \left(\frac{p^2}{2m} + \frac{1}{2}kx^2 \right)} dx dp$$

$$Z = \frac{1}{h} \int_{-\infty}^{+\infty} e^{-\frac{Bp^2}{2m}} dp \int_{-\infty}^{+\infty} e^{-\beta kx^2} dx$$

$$Z = \frac{1}{h} \times \sqrt{\frac{2\pi m}{\beta}} \times \sqrt{\frac{\pi}{\beta}}$$

> Helmholtz Free Energy

$$\text{As we have } \langle E \rangle = U = - \frac{\partial}{\partial \beta} (\ln Z)$$

$$F = U - TS$$

$$\text{or, } \beta F = - \ln(Z)$$

$$\text{or } \beta F = \beta U - TS \times \frac{1}{K_B T}$$

$$\text{or } F = - K_B T \ln Z$$

$$\text{or } \beta F = \beta U - \frac{S}{K_B}$$

$$\boxed{F = - K_B T \ln Z}$$

$$\text{or } \frac{\partial}{\partial \beta} (\beta F) = U = - \frac{\partial}{\partial \beta} (\ln Z)$$

$$\text{Also, } F = U - TS$$

$$\circ dF = dU - TdS - SdT$$

$$\circ dF = TdS - PdV - TdS - SdT$$

$$dF = - PdV - SdT$$

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

Logarithmic Error in Energy Calculation

Partition function. $Z = \sum e^{-\beta E_i}$

$$\ln Z = \ln \left(\sum e^{-\beta E_i} \right)$$

$$\alpha, -\frac{\partial}{\partial \beta} (\ln Z) = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \langle E \rangle$$

Also, $Z = \sum e^{-\beta E_i}$

$$\frac{\partial Z}{\partial \beta} = - \sum E_i e^{-\beta E_i}$$

$$\alpha \frac{\partial^2 Z}{\partial \beta^2} = \sum E_i^2 e^{-\beta E_i}$$

$$\cdot \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \langle E^2 \rangle$$

$$\text{Now. } \langle \langle E \rangle^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left[\frac{\partial}{\partial \beta} (\ln Z) \right]^2 = \frac{\partial^2}{\partial \beta^2} (\ln Z)$$

$$\cdot \langle \langle E \rangle^2 \rangle = \frac{\partial}{\partial \beta} \left[\frac{\partial}{\partial \beta} (\ln Z) \right] = - \frac{\partial}{\partial \beta} (\bar{E})$$

$$\cdot \langle \langle E \rangle^2 \rangle = - \frac{\partial}{\partial T} \left(\frac{\partial \bar{E}}{\partial \beta} \right)$$

$$\cdot \langle \langle E \rangle^2 \rangle = K_B T^2 \frac{\partial}{\partial T} (\bar{E}) = K_B T^2 C_V$$

$$\text{ideal gas. } \bar{E} = \frac{3}{2} N K_B T \Rightarrow \frac{\partial \bar{E}}{\partial T} = \frac{3}{2} N K_B$$

$$\langle \langle E \rangle^2 \rangle = \sqrt{K_B T^2 \times \frac{3}{2} N K_B} = K_B T \sqrt{\frac{3N}{2}}$$

$$\frac{\langle \langle E \rangle^2 \rangle}{E} = \frac{K_B T \sqrt{\frac{3N}{2}}}{\frac{3}{2} N K_B T} \propto \frac{1}{\sqrt{N}} \quad (N \uparrow, \langle \langle E \rangle^2 \rangle \downarrow)$$

(Relative fluctuation)

Fermi Dirac distribution

① Only valid for Fermions.

② No of Particles = n

available state = g

No of possible way of distribution

$$g_{Cn} = \frac{g!}{n! (g-n)!}$$

> No of microstates, $\Omega = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}$

③ Total number of particles will be Constant

$$\sum n_i = N = \text{Constant} \Rightarrow \sum s_{ni} = 0 \text{ but } s_{ni} \neq 0$$

④ Total energy is Constant. $\sum n_i E_i = E = \text{Constant}$

Entropy. $S = K \ln \Omega = K \ln \left[\prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \right]$

a) $S = K \sum (\ln g_i! - \ln n_i! - \ln (g_i - n_i)!)$

a) $S = K \sum (g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i - n_i) \ln (g_i - n_i) + (g_i - n_i))$

c) $S = K \sum g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i)$

For Equilibrium Condition $\delta S = 0$

$$\delta S = K \left[\left(n_i \times \frac{1}{n_i} \ln n_i - (\ln n_i) s_{ni} \right) - \frac{(g_i - n_i)}{(g_i - n_i)} (-s_{ni}) + \ln (g_i - n_i) s_{ni} \right] = 0$$

$$\text{or } \sum g_i s_{ni} - K \sum [\ln(g_i/n_i) s_{ni} - (\ln n_i) s_{ni}] = 0$$

$$\text{or } \sum \left(\ln \frac{g_i/n_i}{n_i} \right) s_{ni} = 0$$

we have Constraint Equation

$$\sum n_i E_i = E$$

$$\text{or } \sum (s_{ni}) E_i = E = 0$$

$$\text{or } \beta \sum E_i (s_{ni}) = 0$$

$$\sum n_i = N$$

$$\text{or } \sum s_{ni} = 0$$

$$\text{or } \alpha \sum s_{ni} = 0$$

Now by applying Lagrange multiplier

$$\sum \left(\ln \frac{g_i/n_i}{n_i} \right) s_{ni} - \alpha \sum s_{ni} - \beta \sum E_i (s_{ni}) = 0$$

$$\sum \left(\ln \frac{g_i/n_i}{n_i} - \alpha - \beta E_i \right) s_{ni} = 0$$

$$\ln \frac{g_i/n_i}{n_i} = \alpha + \beta E_i$$

$$\frac{g_i/n_i}{n_i} = e^{(\alpha + \beta E_i)} \Rightarrow g_i = n_i [1 + e^{(\alpha + \beta E_i)}]$$

Now Probability distribution function

$$\frac{n_i}{g_i} = f(E) = \frac{1}{1 + e^{(\alpha + \beta E_i)}}$$

$$\beta = \frac{1}{kT}$$

$$\alpha = -\frac{\mu}{kT}$$

$$f(E) = \frac{1}{1 + e^{\frac{(\epsilon - \mu)}{kT}}} \Rightarrow \text{only for Fermions}$$

> Fermi Energy. if $\epsilon = \mu$ then

$$f(E) = \frac{1}{2}$$

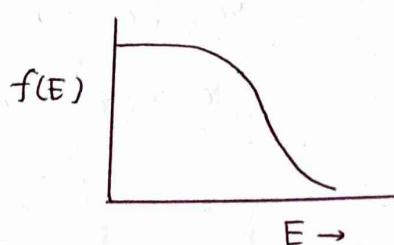
This Energy is Fermi Energy.

> For fermions we have

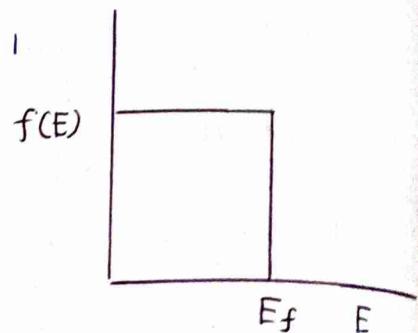
$$f(E) = \frac{1}{1 + e^{\frac{E - E_f}{k_B T}}}$$

at. $T=0K$ $e^{\frac{E - E_f}{k_B \times 0}} = e^{+\infty} (E > E_f)$, $f(E) = 0$

$T=0K$, $E < E_f$, $f(E) = 1$



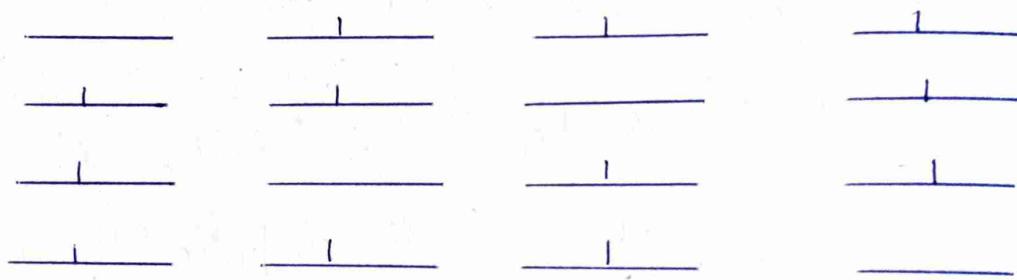
At $T=300K$



At $T=0K$

Fermi Gas in metals

① 3 Fermion and 4 energy state!



At $\rightarrow T=0K$

\leftarrow At $T=+veK$ \rightarrow

> Fermi Level:

$$\frac{1}{\text{---}} \quad \frac{1}{\text{---}} \quad \frac{1}{\text{---}} \quad E_f, n = \frac{N}{2}$$

$$f(E) = 1, \quad E < E_f$$

$$f(E) = 0, \quad E > E_f$$

$$\left. \begin{array}{c} \vdots \\ n < \frac{N}{2} \end{array} \right\} \quad E_f = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{a^3} = \left(\frac{N}{2}\right)^2 \frac{\hbar^2 \pi^2}{2ma^3}$$

$$\frac{1}{\text{---}} \quad \frac{1}{\text{---}} \quad n=3 \\ \frac{1}{\text{---}} \quad \frac{1}{\text{---}} \quad n=2 \\ \frac{1}{\text{---}} \quad \frac{1}{\text{---}} \quad n=1$$

There are $E_f \propto \left(\frac{N}{a}\right)^2$

Fermi Energy $\Rightarrow E_f \propto n_0^2$

(n_0 is number of e^- per unit length)

Now the ground state energy

$$E_0 = \left[\frac{1^2 \pi^2 \hbar^2}{2ma^2} + \frac{2^2 \pi^2 \hbar^2}{2ma^2} + \frac{3^2 \pi^2 \hbar^2}{2ma^2} + \dots + \left(\frac{N}{2}\right)^2 \frac{\pi^2 \hbar^2}{2ma^2} \right] \times 2$$

$$E_0 = \frac{\pi^2 \hbar^2}{2ma^2} \left[1^2 + 2^2 + 3^2 + \dots + \left(\frac{N}{2}\right)^2 \right]$$

$$1^2 + 2^2 + 3^2 + \dots + s^2 = \frac{s(s+1)(2s+1)}{6} \quad (\frac{1}{s} = 0)$$

$$\text{If } s \rightarrow \infty, \quad \frac{s^3 \left(1 + \frac{1}{s}\right) \left(2 + \frac{1}{s}\right)}{6} = \frac{s^3 \times 2}{6} = \frac{s^3}{3}$$

$$\text{So } E_0 = \frac{\pi^2 \hbar^2}{2ma^2} \cdot \frac{1}{3} \left(\frac{N}{2}\right)^3 = \left(\frac{\pi^2 \hbar^2}{24ma^2} N^3\right) N$$

$\therefore E_0 = \frac{E_0}{N} = \frac{\pi^2 \hbar^2 N^2}{24ma^2} \Rightarrow$ Ground state energy per e^\ominus
or Average ground state energy

Fermi energy. $E_f = \frac{\pi^2 \hbar^2 N^2}{8ma^2}$

$$E_0 = \frac{1}{3} E_f$$

$$E_f \text{ ans.}$$

> One dimensional:

$$g(P)dP = \frac{dxdP}{h} = \frac{a}{h} dP = \frac{a}{h} \frac{mdE}{\sqrt{2mE}}$$

$$g(E)dE = \frac{am}{h} \frac{dE}{\sqrt{2mE}} \quad n = \int_0^\infty g(E) f(E)dE$$

$$n = 2 \int_0^{E_f} g(E) f(E) dE + 2 \int_{E_f}^\infty g(E) f(E) dE$$

$$N = 2 \int_0^{E_f} \frac{a}{h} \frac{mdE}{\sqrt{2mE}} = \frac{2ma}{h\sqrt{2m}} \times 2\sqrt{E_f}$$

$$N^2 = \frac{4\pi^2 ma^2 E_f}{h^2 \times 2m} \Rightarrow E_f = \frac{\pi^2 \hbar^2 N^2}{8ma^2}$$

Average Energy:

$$\begin{aligned}
 E_0 &= \int_0^{\infty} E g(E) f(E) dE \\
 &= \int_0^{E_f} E g(E) f(E) dE + \int_{E_f}^{\infty} E g(E) f(E) dE \\
 &= 2 \int_0^{E_f} E \cdot \frac{a}{h} \frac{mdE}{\sqrt{2mE}} dE \quad [f(E)=1] \\
 &= \frac{2am}{h\sqrt{2m}} \int_0^{E_f} \sqrt{E} dE = \frac{2am}{h\sqrt{2m}} \cdot \frac{2}{3} E_f^{3/2}
 \end{aligned}$$

$$\begin{aligned}
 E_0 &= \frac{4am}{h\sqrt{2m}} \cdot \frac{1}{3} E_f^{3/2} \\
 E_0 &= \frac{4am}{h\sqrt{2m}} \cdot \frac{1}{3} \times \sqrt{\frac{\pi h N}{8m\alpha^3}} E_f \\
 E_0 &= \frac{4am}{h\sqrt{2m}} \times \sqrt{\frac{\pi h N}{32\alpha^3 m\alpha^3}} \times \frac{1}{3} E_f \Rightarrow E_0 = \frac{1}{3} E_f
 \end{aligned}$$

3D:

$$g(P)dP = \frac{dxdydz dP_x dP_y dP_z}{h^3}$$

$$g(P)dP = \frac{V \cdot 4\pi P^2 dP}{h^3}$$

$$g(E)dE = \frac{V \cdot 4\pi \cdot 2mE}{h^3} \cdot \frac{mdE}{\sqrt{2mE}}$$

$$N = 2 \int_0^{\infty} g(E) dE f(E)$$

$$= 2 \left[\int_0^{E_f} g(E) f(E) dE + \int_{E_f}^{\infty} g(E) f(E) dE \right]$$

$$N = 2 \int_0^{E_f} \frac{V \cdot 4\pi 2mE}{h^3} \frac{mdE}{\sqrt{2mE}}$$

$$\alpha \frac{N}{V} = n_0 = \frac{16\pi m^2}{h^3} \frac{1}{\sqrt{2m}} \int_0^{E_f} \sqrt{E} dE$$

$$\alpha n_0 = \frac{16\pi m^2}{h^3 \sqrt{2m}} \frac{2}{3} E^{3/2}$$

$$\left(\frac{N}{V}\right)^{3/2} = \left[\frac{16\pi m^2}{h^3 \sqrt{2m}} \frac{2}{3} E^{3/2} \right]^{3/2 \times 2/3}$$

$$\alpha E_f = \frac{\hbar^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3} \Rightarrow E_f \propto \left(\frac{N}{V}\right)^{2/3} \Rightarrow E_f \propto n_0^{2/3}$$

3D Energy: $E_0 = 2 \times \int_0^{\infty} E g(E) f(E) dE$

$$\begin{aligned} E_0 &= 2 \int_0^{E_f} E g(E) dE \\ &= 2 \int_0^{E_f} E \cdot \frac{8\pi V m^2}{h^3 \sqrt{2m}} \sqrt{E} dE \\ &= \frac{16\pi V m^2}{h^3 \sqrt{2m}} \int_0^{E_f} E^{3/2} dE = \frac{16\pi V m^2}{\sqrt{2m} h^3} \frac{2}{5} E_f^{5/2} \end{aligned}$$

$$E_0 = \frac{16\pi V m^2}{\sqrt{2m} h^3} \times \frac{2}{5} \times \left(\frac{\hbar^2}{2m} \right)^{3/2} \frac{3N}{8\pi V} E_f = \frac{3}{5} E_f$$

$$E_f \Big|_{1D} \propto n^{2/1}$$

$$E_0 = \frac{1}{3} E_f = 0.33 E_f \quad (1D)$$

$$E_f \Big|_{2D} \propto n^{2/2}$$

$$E_0 = \frac{1}{2} E_f = 0.5 E_f \quad (2D)$$

$$E_f \Big|_{3D} \propto n^{2/3}$$

$$E_0 = \frac{3}{5} E_f = 0.6 E_f \quad (3D)$$

Bose-Einstein Distribution

For Bosonic Particles.

if n is the no of Particle (indistinguishable)

g is the no of state

then number of microstate.

$$\Omega = \prod_i \frac{(n+g-1)!}{n! (g-1)!}$$

$$S = K \ln \Omega = K \sum (\ln(n+g-1)! - \ln n! - \ln(g-1)!)$$

$$\text{or } \delta S = K \sum \left(\ln \frac{n+g_i}{n_i} \right) \delta n_i = 0$$

$$\sum n_i = N \Rightarrow \alpha \sum \delta n_i = 0 \quad \text{--- (1)}$$

$$\sum n_i E_i = E \Rightarrow \beta \sum E_i \delta n_i = 0 \quad \text{--- (2)}$$

$$\sum \left(\ln \frac{n+g_i}{n_i} - \alpha - \beta E_i \right) \delta n_i = 0$$

$$\text{or } \ln \frac{n+g_i}{n_i} = \alpha + \beta E_i$$

$$\text{or } \frac{n_i}{g_i} = \frac{1}{e^{\frac{(E_i - \mu)}{K_B T}} - 1}$$

$$\alpha = -\frac{\mu}{K_B T}$$

$$\beta = \frac{1}{K_B T}$$

μ is chemical

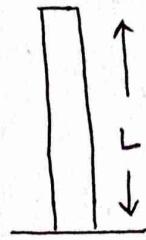
potential

$$n_i = \frac{g_i}{e^{\frac{(E_i - \mu)}{K_B T}} - 1}$$

if $mgl \gg k_B T$ then
find average Energy

\Rightarrow Hamiltonian of the system

$$E = \frac{(P_x^2 + P_y^2 + P_z^2)}{2m} + mgz$$



Partition function of the system

$$\begin{aligned} Z &= \frac{1}{h^3} \int e^{-\beta E} d^3x d^3p \\ &= \frac{1}{h^3} \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m} P_x^2} dP_x \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m} P_y^2} dP_y \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m} P_z^2} dP_z \\ &\quad \int_0^L e^{\beta mgz} dz \int dx dy \\ &= \frac{1}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} A \left[\frac{e^{-mgz\beta}}{-mg\beta} \right]_0^L \\ &= \frac{A}{\beta^3 m g h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} (1 - e^{-mgL\beta}) \\ &= K \times \frac{1}{\beta^{5/2}} = K\beta^{-5/2} \end{aligned}$$

$$\chi_n z = \chi_n K - \frac{5}{2} \chi_n \beta$$

Average Energy

$$\langle E \rangle = - \frac{\partial}{\partial \beta} (\chi_n z) = \frac{5}{2} \frac{1}{\beta} = \frac{5}{2} K T$$

Average Energy of the system is

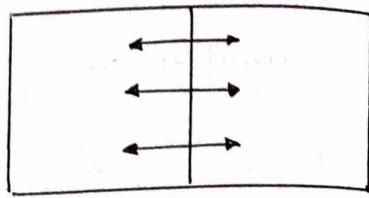
$$\langle E \rangle = \frac{5}{2} K T$$

Thermodynamic Equilibrium

02.04.2024

① Thermal Equilibrium

There is a diathermic wall
so only heat can be transferred
but material cannot.



so total internal energy is const.

$$U^{(1)} + U^{(2)} = \text{Constant}$$

$$\text{or } dU^{(1)} + dU^{(2)} = 0 \Rightarrow dU^{(1)} = -dU^{(2)}$$

Here the overall exchange heat $dS = 0$.

$$TdS = 0$$

$$dS = \frac{\partial S}{\partial U^{(1)}} dU^{(1)} + \frac{\partial S}{\partial U^{(2)}} dU^{(2)}$$

$$\text{or } 0 = \frac{\partial S}{\partial U^{(1)}} dU^{(1)} = \frac{\partial S}{\partial U^{(2)}} dU^{(2)}$$

$$\text{or } 0 = \frac{1}{T^{(1)}} dU^{(1)} - \frac{1}{T^{(2)}} dU^{(1)}$$

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}} \Rightarrow$$

$$T^{(1)} = T^{(2)}$$

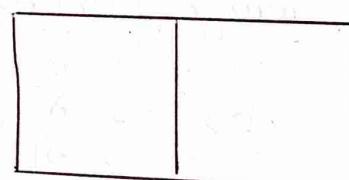
② Mechanical Equilibrium:

The wall is movable
and diathermic

$$U^{(1)} + U^{(2)} = \text{Constant}$$

$$\cdot dU^{(1)} + dU^{(2)} = 0$$

$$\cdot dU^{(1)} = -dU^{(2)}$$



$$V^{(1)} + V^{(2)} = \text{Constant}$$

$$dV^{(1)} + dV^{(2)} = 0$$

$$\cdot dV^{(1)} = -dV^{(2)}$$

Here also $TdS = 0$

$$dS = 0$$

$$dS = \left. \frac{\partial S}{\partial U^{(1)}} \right|_V dU^{(1)} + \left. \frac{\partial S}{\partial V^{(1)}} \right|_U dV^{(1)} + \left. \frac{\partial S}{\partial U^{(2)}} \right|_V dU^{(2)} + \left. \frac{\partial S}{\partial V^{(2)}} \right|_U dV^{(2)}$$

a) $0 = \frac{1}{T^{(1)}} dU^{(1)} + \frac{P^{(1)}}{T^{(1)}} dV^{(1)} - \frac{1}{T^{(2)}} dU^{(2)} - \frac{P^{(2)}}{T^{(2)}} dV^{(2)}$

b) $0 = \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right] dU^{(1)} + \left[\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}} \right] dV^{(1)} = 0$

so here $T^{(1)} = T^{(2)}$ then $\boxed{P^{(1)} = P^{(2)}}$

The diathermic wall will move until their pressure (force became same and net force zero).

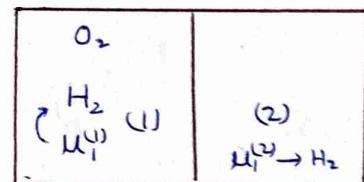
③ Equilibrium with respect to matter flow:

The wall is Semipermeable

So matter can exchange

$$TdS = dU + PdV - \mu dN + Bdm \dots$$

if $dU = 0$
 $dV = 0$ then $ds = -\frac{\mu}{T} dN$



Semi permeable wall can allow to flow one type of materials under concentration gradient.

if $T^{(1)} = T^{(2)}$ $\mu_i \rightarrow$ chemical Potential of 1st material

$$ds = \frac{\mu_i^{(2)} - \mu_i^{(1)}}{T} dN_i^{(1)}$$

if $ds = 0$

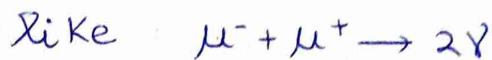
$$dN_i^{(1)} = 0 \quad \boxed{\text{OR}} \quad \mu_i^{(2)} = \mu_i^{(1)}$$

if $ds > 0$ $\mu_i^{(2)} - \mu_i^{(1)} > 0$

$$\mu_i^{(2)} - \mu_i^{(1)} > 0 \quad \boxed{\text{OR}} \quad dN_i^{(1)} < 0$$

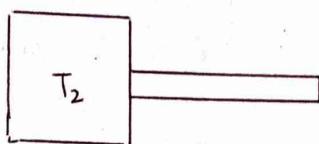
$dN_i^{(1)} > 0$ Transfer of particle occurs from Higher to Lower chemical Potential

where particle created or destroyed, there no calculation for μ .



Entropy of Universe:

A solid at temp T_1 is brought in contact with a heat reservoir at temp T_2 ($T_2 > T_1$)



For the Solid, ΔS_1

$$\Delta S_1 = mc \ln \left(\frac{T_2}{T_1} \right)$$

Change in entropy of the reservoir

$$\Delta S_2 = -\frac{mc(T_2 - T_1)}{T_2}$$

Total change in entropy,

$$\Delta S = \Delta S_1 + \Delta S_2 = mc \ln \left(\frac{T_2}{T_1} \right) - \frac{mc(T_2 - T_1)}{T_2}$$

$$\text{put } 1 - \frac{T_2}{T_1} = x \quad \frac{\Delta S}{mc} = -\ln x - \ln(1-x)$$

$$\frac{\Delta S}{mc} = \left(x + \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4} + \dots \right) - x = \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4}$$

Since $x > 0$

$$\Delta S_u > 0.$$

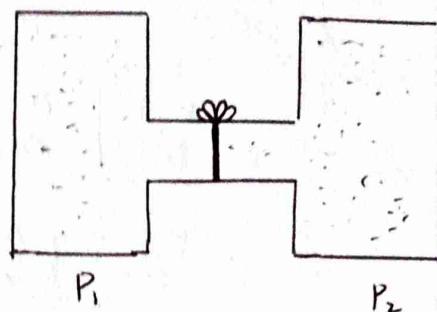
- So. the change in entropy of the universe is positive

Entropy of Mixing:

Initially they have

Pressure P_1 and P_2 . After mixing the pressure became P .

Since temperature is constant



$$\Delta S_1 = -n_1 R \ln \frac{P}{P_1}$$

Entropy of the mixture

$$\Delta S_2 = -n_2 R \ln \frac{P}{P_2}$$

$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$$

$$= -n_1 R \ln \frac{P}{P_1} - n_2 R \ln \frac{P}{P_2}$$

$$= n_1 R \ln \frac{P_1}{P} + n_2 R \ln \frac{P_2}{P}$$

$$= n_1 R \ln x_1 + \ln x_2$$

$$\frac{\Delta S_{\text{mix}}}{n_1+n_2} = \frac{n_1}{n_1+n_2} R \ln x_1 + \frac{n_2}{n_1+n_2} R \ln x_2$$

Δs is Specific Entropy.

$$\boxed{\Delta s = x_1 R \ln x_1 + x_2 R \ln x_2}$$

Enthalpy:

At Constant Pressure, heat supplied to a system is Enthalpy

$$P = \text{Constant} \Rightarrow dP = 0$$

$$dH = Tds + pdV$$

$$H = U + PV$$

$$\text{or } dH = dU + PdV + Vdp$$

$$\text{or } dH = Tds + Vdp$$

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

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

Let for any process $dH = 0$

$$TdS + VdP = 0$$

$$\therefore T \left[\left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT \right] + VdP = 0$$

$$\therefore T \left(\frac{\partial S}{\partial P} \right)_T dP + T \left(\frac{\partial S}{\partial T} \right)_P dT + VdP = 0$$

$$\therefore -T \left(\frac{\partial V}{\partial T} \right)_P dP + C_P dT + VdP = 0$$

$$\text{or } C_P dT = T \left(\frac{\partial V}{\partial T} \right)_P dP - VdP$$

$$\therefore C_P dT = \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP$$

$$\text{or } \left(\frac{\partial T}{\partial P} \right) = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

Joule Thomson

Coefficient

$$\mu = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

Ideal Gas:

$$PV = RT$$

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

$$\mu = \frac{1}{C_P} \left[\frac{RT}{P} - V \right] = \frac{1}{C_P} [V - V] = 0$$

Real Gas

$$(P + \frac{a}{V^2})(V - b) = RT$$

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

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

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

$$\therefore \left(\frac{\partial V}{\partial T} \right)_P = \frac{R(V - b)}{RT - \frac{2a}{V}} \quad (\because V - b \approx V)$$

$$\text{or } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R(V-b)}{RT \left(1 - \frac{2a}{RTV}\right)}$$

$$\therefore T \left(\frac{\partial V}{\partial T}\right)_P = \frac{(V-b)}{\left(1 - \frac{2a}{RTV}\right)}$$

$$\text{or } T \left(\frac{\partial V}{\partial T}\right)_P = (V-b) \left(1 - \frac{2a}{RTV}\right)^{-1}$$

$$\therefore T \left(\frac{\partial V}{\partial T}\right)_P = (V-b) \left(1 + \frac{2a}{RTV}\right)$$

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

Joule Thomson Coefficient

$$\left(\frac{\partial T}{\partial P}\right) = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

$$= \frac{1}{C_P} \left[V + \frac{2a}{RT} - b - V \right] = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right]$$

$$\text{if } u=0 \quad \frac{2a}{RT} - b = 0$$

$$\Rightarrow T = \frac{2a}{Rb}$$

T_i is
inversion
temperature

$$\text{if } T > \frac{2a}{Rb}, \quad \frac{\partial T}{\partial P} = -\text{ve} \quad \Rightarrow \text{Heating occurs}$$

$$T < \frac{2a}{Rb}, \quad \frac{\partial T}{\partial P} = +\text{ve} \quad \Rightarrow \text{Cooling occurs}$$

$T > T_i \Rightarrow JT$ Heating occurs

$T < T_i \Rightarrow JT$ Cooling occurs

① For a particular thermodynamic system the entropy of the system is $S = CV^{1/4}U^{3/4}$. The Gibbs potential for the system is

$$\Rightarrow S = CU^{3/4}V^{1/4} \quad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$$G_1 = U - TS + PV$$

$$\frac{3}{4}U^{-1/4}T^{1/4} = \frac{1}{T}$$

$$\text{or } T = \frac{4}{3C}U^{1/4}/V^{1/4}$$

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

$$\text{or } ST = \frac{4}{3C}\left(\frac{U}{V}\right)^4 \times CU^{3/4}V^{1/4}$$

$$\text{or } P = T\left(\frac{\partial S}{\partial V}\right)$$

$$\text{or } ST = \frac{4}{3}U$$

$$P = T \times \frac{1}{4}V^{-3/4}CU^{3/4}$$

$$PV = T \times \frac{1}{4}V^{1/4}CU^{3/4} = \frac{U}{3}$$

$$G_1 = U - TS + PV = U - \frac{4}{3}U + \frac{U}{3} = 0$$

② Helmholtz Free energy of a system is given by

$$F = A + BT(1 - \lambda nT) - CT\lambda nV.$$

$$\Rightarrow P = -\left(\frac{\partial F}{\partial V}\right) = \frac{CT}{V}$$

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right) = B(1 - \lambda nT) + BT\left(-\frac{1}{T}\right) - C\lambda nV \\ &= -(B - B\lambda nT - B - C\lambda nV) = +B\lambda nT + C\lambda nV \end{aligned}$$

$$\begin{aligned} U &= F + TS = A + BT(1 - \lambda nT) - CT\lambda nV + BT\lambda nT + CT\lambda nV \\ &= A + BT \end{aligned}$$

$$H = U + PV = A + BT + CT$$

$$G_2 = H - TS = A + BT + CT - TB\lambda nT - TC\lambda nV$$

③ One mole of Van der waal gas $(\frac{\partial T}{\partial V})_U$ is

\Rightarrow Entropy. $S = S(T, V)$

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

$$\alpha \quad TdS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\alpha \quad dU + PdV = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\alpha \quad PdV = C_V dT + \frac{RT}{V-b} dV$$

$$\alpha \quad P = C_V \left(\frac{\partial T}{\partial V}\right)_U + \frac{RT}{V-b}$$

$$\alpha \quad \left[P - \frac{RT}{V-b}\right] \frac{1}{C_V} = \left(\frac{\partial T}{\partial V}\right)_U$$

$$\left[\frac{RT}{V-b} - \frac{a}{V^2}\right] \frac{1}{C_V} = \left(\frac{\partial T}{\partial V}\right)_U \Rightarrow \left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V V^2}$$

Thermal Conductivity

Rate of heat Energy transfer

$$\frac{Q}{t} \propto \frac{A(T_1 - T_2)}{\lambda}$$

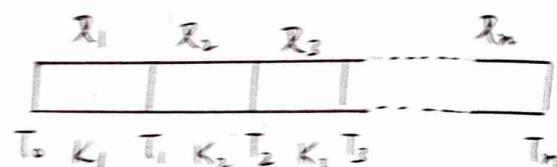
$$\frac{Q}{t} = KA \frac{dT}{dx} \Rightarrow H = KA \frac{dT}{dx}$$



Series Combination

Here are f

Cross section is
Same



$$\frac{dS}{dt} = K_1 A \frac{T_0 - T_1}{\lambda_1}$$

$$\frac{dS}{dt} = K_2 A \frac{T_{n-1} - T_n}{\lambda_n}$$

$$\frac{dS}{dt} = K_2 A \frac{T_1 - T_2}{\lambda_2}$$

$$\frac{dS}{dt} = K_{eq} A \frac{T_0 - T_N}{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}$$

$$\frac{dS}{dt} = K_{eq} A \frac{T_0 - T_N}{(\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n)}$$

$$T_0 - T_1 = \frac{\lambda_1}{K_1 A} \frac{dS}{dt} \quad T_1 - T_2 = \frac{\lambda_2}{K_2 A} \frac{dS}{dt}$$

$$T_0 - T_N = \frac{(\lambda_1 + \lambda_2 + \dots + \lambda_n)}{K_{eq} A} \frac{dS}{dt}$$

$$T_0 - T_1 + T_1 - T_2 + T_2 - T_3 + \dots + T_{n-1} - T_n = (\sum \lambda_i) \frac{dS}{dt} \cdot \frac{1}{K_{eq} A}$$

$$\left(\frac{\lambda_1}{K_1 A} + \frac{\lambda_2}{K_2 A} + \dots + \frac{\lambda_n}{K_n A} \right) \frac{dS}{dt} = (\sum \lambda_i) \frac{dS}{dt} \cdot \frac{1}{K_{eq} A}$$

Series:

$$K_{eq} = \frac{\sum \lambda_i}{\sum \frac{\lambda_i}{K_i}}$$

Parallel

$$K_{eq} = \frac{\sum K_i A_i}{\sum A_i}$$

- ① Find the grand Partition function of a photon gas
(JEST- 2012)

\Rightarrow Canonical Partition function for 3D

$$Z_N = \frac{1}{h^3} \int e^{-\beta H} d^3 p d^3 x = \frac{V}{h^3} \int e^{-\beta H} 4\pi p^2 dp$$

$$\text{For a photonic gas } E = pc \Rightarrow p = \frac{E}{c}$$

$$Z_N = \frac{4\pi V}{h^3} \int e^{-\beta pc} \frac{E^2}{c^2} \frac{dE}{c}$$

$$Z_N = \frac{4\pi V}{h^3 c^3} \int_0^\infty e^{-\beta E} E^2 dE = \frac{2 \times 4\pi V}{h^3 c^3 \beta^3} = \frac{8\pi V}{(hc\beta)^3}$$

Grand canonical Partition function

$$Z_{\mu} = \exp \left[e^{\mu/kT} Z_N \right] = \exp \left[\frac{\mu}{kT} \frac{8\pi V}{(hc\beta)^3} \right]$$

- ② 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 two energy state. Find Entropy

\Rightarrow Canonical Partition Function (JEST- 2012)

$$Z = \sum g_1 e^{-\beta E_1} + \sum g_2 e^{-\beta E_2}$$

$$P_1 = \frac{\sum g_1 e^{-\beta E_1}}{Z} \Rightarrow \ln P_1 = \ln g_1 - \beta E_1 - \ln Z$$

$$\Rightarrow \ln \left(\frac{P_1}{g_1} \right) = -\beta E_1 + \frac{F}{kT} = -\beta E_1 + \beta F$$

$$\Rightarrow \ln \left(\frac{P_1}{g_1} \right) = \beta (F - U) = -\beta X TS$$

$$\Rightarrow \ln \left(\frac{P_1}{g_1} \right) = -\frac{S}{K} \Rightarrow S = -K \ln \frac{P_1}{g_1}$$

$$S = -K \left[P_1 \ln \frac{P_1}{g_1} + P_2 \ln \frac{P_2}{g_2} \right]$$

③ A Collection of N two-levels with energies 0 and E.
if $T \rightarrow \infty$. find the Specific heat

\Rightarrow Partition Function $Z = \sum e^{-\beta E_i}$

$$Z = 1 + e^{-\beta E} \Rightarrow \ln Z = \ln(1 + e^{-\beta E})$$

$$U = -\frac{\partial}{\partial \beta} (\ln Z) = \frac{E e^{-\beta E}}{(1 + e^{-\beta E})}$$

$$\text{Specific heat } C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\frac{E^2}{kT^2} e^{-E/kT}}{(1 + e^{-E/kT})^2}$$

if $T \rightarrow \infty \quad C_V \rightarrow 0$

④ A thermally insulated ideal gas of volume V_1 and temperature T expands to another enclosure of volume V_2 through porous plug. change in temp?

$$\Rightarrow H = U + PV$$

$$\therefore dH = dU + PdV + VdP = TdS + VdP$$

$$\text{In JT effect } dH = TdS = 0 \quad \text{so } VdP = 0$$

$$dW = PdV \Rightarrow nRdT = PdV$$

$$\Rightarrow \Delta T = T \int \frac{dV}{V} \Rightarrow \Delta T = T \ln\left(\frac{V_2}{V_1}\right)$$

⑤ Consider three situations of 4 Particles in 1D Box of width L. If they are Fermions, bosons Classical. then energy?

\Rightarrow If they are Fermion

$$E_F = \frac{\hbar v \tilde{\lambda}}{2m \lambda^2} \sum_{i=1}^4 \tilde{n}_i = 30 \times \frac{\hbar v \tilde{\lambda}}{2m \lambda^2}$$

$$E_B = E_d = 4 \times \frac{\hbar v \tilde{\lambda}}{2m \lambda^2} \quad E_F > E_B = E_d$$

(6)

Ice of density s_1 melts at Pressure P and absolute temperature T to form water of density s_2 . What is the change in internal energy (JEST 2014)

$$\Rightarrow dU = dQ - dW = mL - PdV$$

$$V = \frac{L}{s} \Rightarrow dV = -\frac{1}{s} ds$$

$$dU = L - \int_{s_1}^{s_2} \left(-\frac{1}{s} \right) ds = L + P \left[\frac{1}{s_1} - \frac{1}{s_2} \right]$$

(7)

A particle in thermal eqm. $-E, 0, E$. If the system is maintained at a temperature $T \gg \frac{E}{k_B}$ Then average energy

$$\Rightarrow \text{Partition function } Z = 1 + e^{-\beta E} + e^{\beta E}$$

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial \beta} (\ln Z) = -\frac{\partial}{\partial \beta} \left[\ln (1 + e^{-\beta E} + e^{\beta E}) \right] \\ &= -\frac{(-E e^{-\beta E} + E e^{\beta E})}{1 + e^{-\beta E} + e^{\beta E}} = E \left[\frac{e^{-\frac{E}{KT}} - e^{\frac{E}{KT}}}{1 + e^{-\frac{E}{KT}} + e^{\frac{E}{KT}}} \right] \\ &= E \left[\frac{\left(1 - \frac{E}{KT}\right) - \left(1 + \frac{E}{KT}\right)}{1 + \left(1 - \frac{E}{KT}\right) + \left(1 + \frac{E}{KT}\right)} \right] = -\frac{2E^2}{3KT} \end{aligned}$$

(8)

For a quantum mechanical harmonic oscillator

$E_n = (n + \frac{1}{2}) \hbar \omega$. The Partition function is

$$\begin{aligned} \Rightarrow Z &= \sum e^{-\beta E_i} = e^{-\frac{\hbar \omega}{2KT}} + e^{-\frac{3\hbar \omega}{2KT}} + e^{-\frac{5\hbar \omega}{2KT}} + e^{-\frac{7\hbar \omega}{2KT}} \\ &= e^{-\frac{\hbar \omega}{2KT}} \left[1 + e^{-\frac{\hbar \omega}{KT}} + e^{-\frac{2\hbar \omega}{KT}} + \dots \right] = \frac{e^{-\hbar \omega / 2KT}}{1 - e^{\frac{\hbar \omega}{KT}}} \\ &= \frac{e^{\frac{\hbar \omega}{2KT}}}{(e^{\frac{\hbar \omega}{KT}} - 1)} \end{aligned}$$

① A proton of energy 1 MeV is scattered through 180° by a gold nucleus ($Z = 79$). The distance of closest approach is

\Rightarrow For proton $Z = 1$

$$KE = \frac{1}{4\pi\epsilon_0} \frac{ze^2}{r}$$

$$r = \frac{1}{4\pi\epsilon_0} \frac{ze^2}{KE} = 9 \times 10^9 \times \frac{79 \times (1.6 \times 10^{-19})^2}{1.6 \times 10^{-19} \times 10^6} = 113 \text{ fm}$$

The state of an ideal gas is changed through an isothermal process at temperature T . The work done by gas in going from state B to C is double the work done by gas in going from A to B. If the pressure in state B is $\frac{P_0}{2}$, then pressure at C is

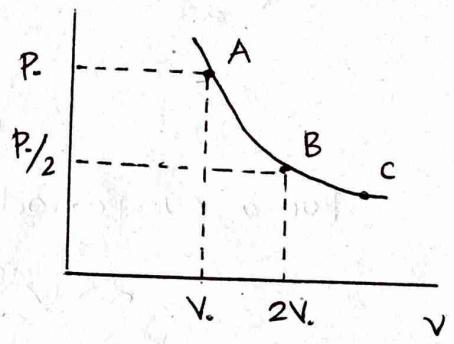
AB is isothermal process

$$P_0 V_0 = \frac{P_0}{2} \times 2V_0 \Rightarrow V_B = 2V_0$$

$$W_{AB} = nRT \cdot \ln\left(\frac{P_A}{P_B}\right)$$

$$W_{BC} = nRT \left(\frac{P_B}{P_C}\right)$$

$$P_C = \frac{P_0}{8}$$



$$W_{BC} = 2W_{AB}$$

$$2 \ln\left(\frac{P_B}{P_C}\right) = 2 \ln\left(\frac{P_A}{P_B}\right)$$

An ideal gas at Pressure P is heated to twice its temp. keeping its volume constant. It is then cooled its original temp at constant pressure. Then work done will be

$$\Rightarrow \frac{PT}{V} \longrightarrow \frac{P'2T}{V}$$

$$PV = nRT$$

$$P'V = nR(2T)$$

$$P' = 2P$$

Isochoric Process $w=0$

$$\frac{P'2T}{V} \longrightarrow \frac{2P,T}{\frac{V}{2}}$$

work done in Constant Pressure

$$w = P \Delta V = 2P(V - \frac{V}{2}) = PV$$

A vessel has two compartment of Volume V_1 and V_2 containing ideal gas at pressure P_1 and P_2 and temp T_1 and T_2 respectively. Wall separating the compartments are removed then

\Rightarrow

$P_1 V_1 T_1$	$P_2 V_2 T_2$
N_1	N_2

$$U_1 + U_2 = U_f$$

$$\frac{f_1}{2} n_1 R T_1 + \frac{f_2}{2} n_2 R T_2 = \frac{f}{2} (n_1 + n_2) R T_f$$

$$\frac{n_1 R T_1 + n_2 R T_2}{(n_1 + n_2) R} = T_f$$

$$\frac{P_1 V_1 + P_2 V_2}{\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2}} = T_f$$

$$\text{Also } P_f (V_1 + V_2) = (n_1 + n_2) R T_f$$

$$P_f = \frac{(n_1 + n_2) R}{V_1 + V_2} \cdot \frac{P_1 V_1 + P_2 V_2}{\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2}}$$

$$P_f = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2}$$

Equipartition Theorem

The energy associated with each dof per molecule is $\frac{1}{2} K_B T$.

If Hamiltonian $H \propto x^n$

$$\text{then Energy } E = \frac{K_T}{n}$$

- ① Consider a one-dimensional gas of N non-interacting particle of mass m $H = \frac{P^2}{2m} + \frac{1}{2} m\omega^2(x^2 + z^2)$
Specific heat in unit of R

$$\Rightarrow H = \frac{P^2}{2m} + \frac{1}{2} m\omega^2(x^2 + z^2)$$

$$E = \frac{1}{2} K_T + \frac{K_T}{2} + \frac{K_T}{1} = 2K_T$$

$$\text{for } N \text{ particle } E = 2NKT$$

$$C_V = \frac{\partial E}{\partial T} = 2NK = 2R$$

* For free expansion of Surrounding $\Delta S = 0$

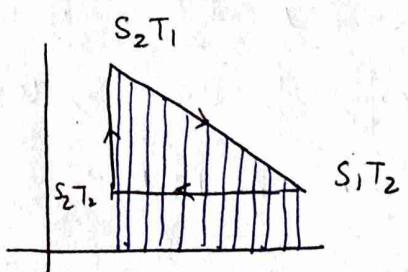
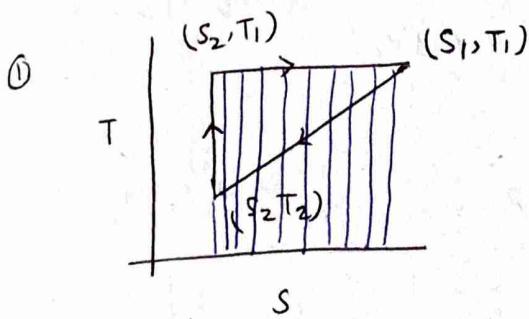
- ② In a certain process $T \propto \frac{1}{S^2}$. If the heat capacity in terms of entropy for the process is $-S/n$.
The value of n is

$$\begin{aligned} \Rightarrow T \propto \frac{1}{S^2} & \quad C = T \left(\frac{\partial S}{\partial T} \right) & \frac{dT}{dS} = -\frac{2K}{S^3} \\ TS^2 = K & \quad = -\frac{TS^3}{2K} & \frac{dS}{dT} = -\frac{S^3}{2K} \\ T = \frac{K}{S^2} & \quad = -\frac{TS^3}{2TS^2} = -S/n \end{aligned}$$

- ③ In free path. if temperature increases, pressure will also increase

$$\lambda = \frac{K_T}{\sqrt{2\pi d^3 p}}$$

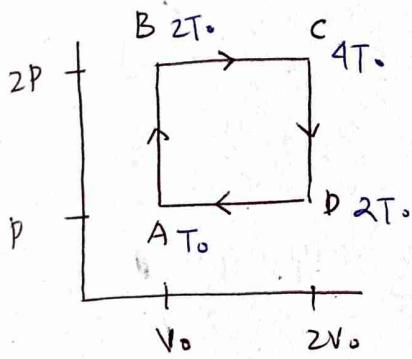
Mean free path remain same



Compare their efficiency $w_1 = w_2$ = Area Same

$$\Rightarrow \text{Efficiency } \eta = \frac{w}{Q_1} = \eta \propto \frac{1}{Q_1}$$

$$Q_1 > Q_2 \quad \therefore \eta_1 < \eta_2$$



Helium gas goes through a cycle ABCDA as shown in figure. the efficiency will be

$$\Rightarrow P_0 V_0 = R T_0$$

$$\Delta Q_{AB} = \Delta U_{AB} + \cancel{\Delta W_{AB}} \quad (\forall \text{ constant})$$

$$= C_V \Delta T = \frac{3}{2} R \times T = \frac{5}{2} R T_0 \quad \text{--- (1)}$$

$$\Delta Q_{BC} = \Delta U_{BC} + \Delta W_{BC}$$

$$= \frac{3}{2} R (4T_0 - 2T_0) + 2P_0 V_0 = 3RT_0 + 2RT_0 = 5RT_0 \quad \text{--- (2)}$$

$$\Delta Q_{CD} = \Delta U_{CD} + \Delta W_{CD} = \frac{3}{2} R (2T_0 - 4T_0) = -3RT_0 \quad \text{--- (3)}$$

$$\Delta Q_{DA} = \Delta U_{DA} + \Delta W_{DA} = \frac{3}{2} R (T_0) + P_0 V_0 = -\frac{5}{2} 12T_0$$

$$Q_1 = \frac{3}{2} R T_0 + \frac{5}{2} 12T_0 = \frac{13}{2} R T_0 = \frac{13}{2} P_0 V_0$$

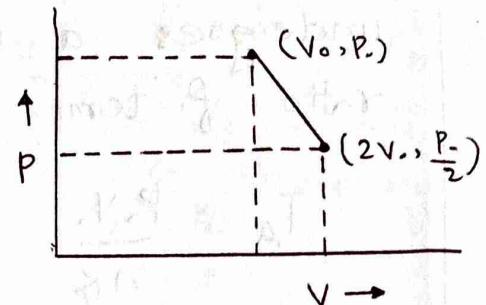
$$\text{Area} \approx w = P_0 V_0$$

① One mole of a gas expands. The maximum temperature in the process.

$$\gamma P - \gamma_1 = \frac{\gamma_2 - \gamma_1}{x_2 - x_1} (x - x_1)$$

$$P - P_0 = \frac{P_0/2 - P_0}{2V_0 - V_0} (V - V_0)$$

$$P = -\frac{P_0}{2V_0} V + \frac{3}{2} P_0$$



$$PV = RT$$

$$P = \frac{RT}{V}$$

$$\frac{RT}{V} = -\frac{P_0}{2V_0} V + \frac{3}{2} P_0 \Rightarrow T = -\frac{P_0}{2V_0 R} V^2 + \frac{3}{2} \frac{P_0}{R} V$$

For $T = T_{\max}$ $\frac{\partial T}{\partial V} = 0 \Rightarrow -2V \frac{P_0}{2V_0 R} = \frac{3}{2} \frac{P_0}{R} = 0$

$$V = \frac{3}{2} V_0$$

② For the Process the ratio $\Delta Q : \Delta W$ is

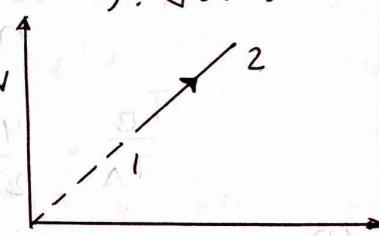
$$V \propto T \Rightarrow P = \text{Constant}$$

$$\Delta Q = \Delta U + \Delta W$$

$$\frac{\Delta Q}{\Delta W} = \frac{nC_p \Delta T}{nR \Delta T} = \frac{C_p}{R}$$

$$C_p = \frac{\gamma R}{\gamma - 1}$$

$$\Delta Q : \Delta W = \gamma : \gamma - 1$$



$$\frac{C_p}{R} = \frac{\gamma}{\gamma - 1}$$

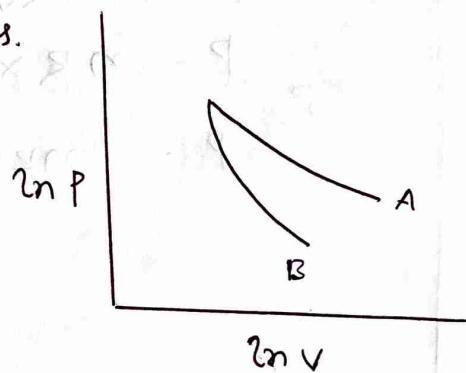
③ Both goes adiabatic process.

In adiabatic Process,

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

$$\gamma_{\text{mono}} > \gamma_{\text{dia}}$$

$$m_B > m_A \Rightarrow \gamma_B > \gamma_A$$



B : mono atomic
A : di atomic

① For a gaseous system, $PV^{5/3} = K$ find work done if volume expands from V_A to V_B

⇒ work done,

$$P_A V_A^{5/3} = K \quad P_B V_B^{5/3} = K$$

$$W = \int_{V_A}^{V_B} P dV = K \int_{V_A}^{V_B} V^{-5/3} dV = -\frac{3}{2} K [V_B^{-2/3} - V_A^{-2/3}]$$

$$= -\frac{3}{2} [P_B V_B^{5/3} V_B^{-2/3} - P_A V_A^{5/3} V_A^{-2/3}]$$

$$= -\frac{3}{2} [P_B V_B - P_A V_A]$$

③ In an adiabatic Process volume changes from V to αV . If the initial Pressure is P then find the final Pressure

$$\Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$V_2 = \alpha V \\ V_1 = V$$

$$P V^\gamma = P_2 (\alpha V)^\gamma \Rightarrow P = P_2 \alpha^\gamma$$

$$W = \frac{P_2 V_2 - P_1 V_1}{1-\gamma} = \frac{P_2 V (\alpha - \alpha^\gamma)}{1-\gamma}$$

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

③ $P = \frac{\alpha T - \beta T^2}{V}$. The work done by the gas if the temperature changes from T_1 and T_2 ($P = \text{constant}$)

$$W = \int P dV$$

$$PV = \alpha T - \beta T^2$$

$$PdV = \alpha dT - 2\beta T dT$$

$$T_1 = \alpha (T_2 - T_1) - \beta (T_2^2 - T_1^2)$$

① A monoatomic ideal gas at 170°C is adiabatically compressed to 1/8 of its original volume. The temperature after compression is (Jest 2012)

⇒ For monoatomic $\gamma = 4/3$

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

$$V_2 = \frac{V_1}{8} \quad T_1 = 443\text{K}$$

$$\Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 443 \times 8^{4/3} = 886\text{K}$$

② Consider a system of particles in 3D with momentum \vec{p} and energy $E = c|\vec{p}|$. The system is maintained at inverse temperature β , volume V and chemical potential μ . Find grand Partition function (Jest 2012)

⇒ Canonical Partition function

$$Z = \frac{1}{h^3} \int e^{-\beta E} d^3x d^3p = \frac{1}{h^3} \int e^{-\beta cp} 4\pi p^2 dp \int d^3x$$

$$Z = \frac{V}{h^3} \cdot 4\pi \int_0^\infty e^{-\beta cp} \cdot p^2 dp \quad \beta cp = t \quad p = \frac{t}{\beta c}$$

$$Z = \frac{4\lambda V}{h^3} \int_0^\infty e^{-t} \frac{t^2}{(\beta c)^2} \frac{dt}{\beta c} \quad dt = \frac{dt}{\beta c}$$

$$Z = \frac{4\lambda V}{h^3} \cdot \frac{1}{(\beta c)^3} \int_0^\infty e^{-t} t^{3/2} dt = \frac{4\lambda V}{h^3} \cdot \frac{\Gamma(3/2)}{(\beta c)^3} = \frac{8\lambda V}{(h\beta c)^3}$$

Grand Partition function —

$$Z_G = \exp(e^{\mu\beta} Z)$$

$$= \exp\left(e^{\mu\beta} \frac{8\lambda V}{(h\beta c)^3}\right)$$

$2dU + 3dW = 0$ represents which process?

$$\Rightarrow 2dU + 3dW = 0$$

$$f \frac{dT}{T} = -3 \frac{dV}{V}$$

$$2C_V dT + 3PdV = 0$$

$$T^{\frac{f}{3}} = K$$

$$2 \frac{f}{2} RT dT + 3 \frac{RT}{V} dV = 0$$

$$fRdT + 3RT \frac{dV}{V} = 0$$

No process

) Volume, $V = aT^{-1}$. The amount of heat received by the gas if the temp. of the gas increases by ΔT .

$$\Rightarrow dQ = dU + dW$$

$$\frac{V}{T} = a$$

$$dV = -\frac{a}{T^2} dT$$

$$= C_V dT + PdV$$

$$= \frac{RdT}{\gamma-1} + \frac{RT}{V} \left(-\frac{a}{T^2} dT \right)$$

$$= \frac{RdT}{\gamma-1} - RdT - \frac{RdT(1-\gamma+1)}{\gamma-1} = \frac{RdT(2-\gamma)}{\gamma-1}$$

5) An ideal gas expands as $P = P_0 e^{-\alpha V}$. A

Find the maxm temp. that it will attain in the process

$$\Rightarrow P = P_0 e^{-\alpha V}$$

$$\frac{dT}{dV} = \frac{P}{R} \left(\frac{d}{dV} e^{-\alpha V} \right) = \frac{P}{R} e^{-\alpha V} \cdot (-\alpha) V = \frac{P}{R} e^{-\alpha V} \cdot \frac{-\alpha V}{V} = \frac{P}{R} e^{-\alpha V} \cdot \frac{-\alpha}{V}$$

$$T_{\max} = \frac{P e^{-1}}{\alpha R} = \frac{P}{e \alpha R}$$

④ Two moles of an ideal monoatomic gas undergoes a cyclic process ABCA. Find the ratio of temp at B and A

$$T_A = \frac{P_0 V_0}{nR}$$

$$T_B = \frac{P_B V_B}{nR}$$

$$T_B = \frac{3P_0}{nR} V_B$$

$$\tan 30^\circ = \frac{2P_0}{V_B - 6V_0}$$

$$\tan 60^\circ = \frac{3P_0 - P_0}{V_B - V_0}$$

$$-V_B + 6V_0 = 3V_B - 3V_0 \quad V_B = \frac{2P_0 + \sqrt{3}V_0}{\sqrt{3}}$$

$$\therefore V_B = 4V_0 \Rightarrow V_B = \frac{9}{4}V_0$$

$$T_A = \frac{P_0 V_0}{nR} \quad T_B = \frac{3P_0 \frac{9}{4}V_0}{nR} = \frac{27}{4} \frac{P_0 V_0}{nR}$$

$$\frac{T_B}{T_A} = \frac{4}{27}$$

⑤ 2 mole of a gas. Find the pressure at point A

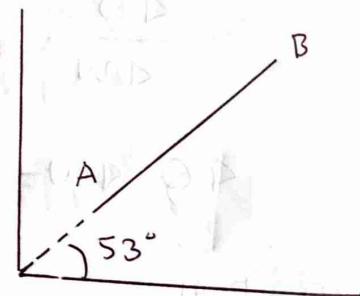
\Rightarrow

$$PV = nRT$$

$$P = nR \left(\frac{T}{V} \right)$$

$$P = nR \times \frac{1}{\text{slope}}$$

$$P = nR \times \cot 53^\circ = 2 \times 8.314 \times \frac{3}{4 \times 10^{-3}}$$



③ 1 mol of a monoatomic gas is initially at constant temp T_0 . It expands from a volume V_0 to $2V_0$ under constant pressure. Absorbed heat

$$\begin{aligned} \Rightarrow \Delta Q &= \Delta U + \Delta W \\ &= C_p \Delta T + P \Delta V \\ &= C_V(2T_0 - T_0) + P(2V_0 - V_0) \\ &= C_V T_0 + PV_0 = \frac{3}{2} R T_0 + RT_0 = \frac{5}{2} R T_0 \end{aligned}$$

④ A monoatomic gas is described by the eqn of state $P(V - bn) = nRT$. The max^m density is moles per unit volume to which the gas can be compressed is

$$\begin{aligned} \Rightarrow \frac{dP}{dV} &= 0 \\ \frac{RT + Pb - Pb}{(RT + Pb)^2} &= 0 \Rightarrow RT = 0 \\ \Rightarrow \rho_{\max} &= \frac{n}{V} = \frac{P}{RT + Pb} \\ &= \frac{P}{0 + Pb} = \frac{1}{b} \end{aligned}$$

⑤ A perfect monoatomic gas undergoes reversible adiabatic expansion. Relation b/w U and V

$$\begin{aligned} \Rightarrow dU &= -dw \\ dU &= -PdV \\ \int dU &= -\int K V^{-\gamma} dV \Rightarrow U = -K \frac{V^{-\gamma+1}}{-\gamma+1} \\ UV^{2/3} &= K' \quad UV^{1-\gamma} = K! \Rightarrow UV^{-1+\frac{5}{3}} = K! \end{aligned}$$

for an ideal gas $PV^{\gamma} = \text{const}$. volume decreases then temperature also decreases

$$PV^{\gamma} = K$$

$$\frac{RT}{V^{\gamma}} = K$$

$$T \propto V^{\gamma}$$

③ Efficiency of a perfectly reversible heat engine operating between absolute temperature T and zero is equal to (Jest 2012)

$$\Rightarrow \text{Efficiency. } \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{0}{T} = 1$$

④ Consider an ideal gas of mass m at temperature T_1 , mixed isobarically with equal mass of same gas at temperature T_2 in a thermally insulated container. The change in entropy of universe (Jest 2012)

\Rightarrow If T_f be the final temperature -

$$m_1 C_{p_1} (T_1 - T_f) + m_2 C_{p_2} (T_2 - T_f) = 0$$

As $m_1 = m_2$ and $C_{p_1} = C_{p_2}$ then

$$T_1 + T_2 = 2T_f \Rightarrow T_f = \frac{1}{2} (T_1 + T_2)$$

Now change in entropy at constant pressure -

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = m C_p \ln \left(\frac{T_f}{T_1} \right) + m C_p \ln \left(\frac{T_f}{T_2} \right) \\ &= m C_p \ln \left[\frac{T_1 + T_2}{2T_1} \right] + m C_p \ln \left[\frac{T_1 + T_2}{2T_2} \right] \\ &= m C_p \ln \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right] = 2m C_p \ln \left[\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right] \end{aligned}$$

⑤ A collection of N two-level systems with energies 0 and $E > 0$ is in thermal eqbm at temperature T . For $T \rightarrow \infty$ Specific heat approaches to (Jest 2012)

\Rightarrow Partition function $Z = 1 + e^{-\beta E}$

$$\chi_n Z = \chi_n (1 + e^{-\beta E})$$

$$\frac{\partial}{\partial \beta} (\chi_n Z) = \left(\frac{-E e^{-\beta E}}{1 + e^{-\beta E}} \right)$$

$$U = -\frac{\partial}{\partial \beta} (\chi_n z) = \left(\frac{E e^{-\beta E}}{1 + e^{-\beta E}} \right) = \left(\frac{E e^{-\frac{E}{kT}}}{1 + e^{-\frac{E}{kT}}} \right)$$

Specific heat $C_V = \left(\frac{\partial U}{\partial T} \right)_V$

$$C_V = E \frac{(1 + e^{-\frac{E}{kT}}) \left(-\frac{E}{k} \right) e^{-\frac{E}{kT}} - e^{-\frac{E}{kT}} \left(-\frac{E}{k^2} \right) e^{-\frac{E}{kT}}}{(1 + e^{-\frac{E}{kT}})^2}$$

$$\text{As } C_V \Big|_{T \rightarrow \infty} = 0$$

A thermally insulated ideal gas of volume V_1 and temperature T expands to another enclosure of volume V_2 through a porous plug. The change in temperature of the gas (Jest 2012)

=) Here Enthalpy $H = \text{constant}$

$$H = U + PV \Rightarrow dH = dU + PdV + VdP = Tds + Vdp$$

As thermally insulated $Tds = 0$, $dH = 0$, $Vdp = 0$

$$nRdT = PdV + V \cancel{dp} \Rightarrow nRdT = PdV \Rightarrow T \chi_n \frac{V_2}{V_1} = \Delta T$$

) 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)

$$dQ = dU + dw \quad dQ - nC_p \Delta T = \frac{7}{2} R \Delta T$$

$$\left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_V + R \quad dw = R$$

$$C_p - C_v = R \quad \frac{dQ}{dw} = \frac{7}{2} \Rightarrow \frac{dw}{dQ} = \frac{2}{7}$$

) What is the contribution of the conduction electrons in the molar entropy of a metal with electronic coefficient of specific heat? (Jest 2013)

$$=) \text{ Specific heat } C_V = AT + BT^3$$

- ⑤ A metal bullet comes to rest after hitting its target with a velocity 80 m/s. If 50% of the heat generated remains in bullet, what is increase in temperature? (Specific heat = 160 Joule/Kg°C) (Jest 2013)

$$\Rightarrow W = mgh \Rightarrow \frac{1}{2}mv^2 = \frac{1}{2}m \times 80^2 = 3200 \text{ Joule}$$

$$50\% \text{ of it} : 3200 \times \frac{50}{100} = 1600 \text{ J} \cdot mc \Delta T \\ 1600 = 160 \Delta T \Rightarrow \Delta T = 10^\circ\text{C}$$

- ⑥ 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 is given by (Jest 2014)

\Rightarrow Partition function

$$Z = \sum e^{-\beta E_i} = e^0 + e^{-\beta E} = (1 + e^{-\beta E})$$

$$\mathcal{R}_n Z = \mathcal{R}_n (1 + e^{-\beta E}) \Rightarrow \frac{\partial}{\partial \beta} (\mathcal{R}_n Z) = \frac{-E e^{-\beta E}}{1 + e^{-\beta E}}$$

$$\text{Internal energy} \Rightarrow U = - \frac{\partial}{\partial \beta} (\mathcal{R}_n Z) = \frac{E e^{-\beta E}}{(1 + e^{-\beta E})}$$

$$\text{So, } C_V = \left(\frac{\partial U}{\partial T} \right)_V = E \frac{\partial}{\partial T} \left[\frac{e^{-\frac{E}{kT}}}{1 + e^{-\frac{E}{kT}}} \right] \\ = E \left\{ \frac{(1 + e^{-\frac{E}{kT}})(-\frac{E}{kT}) e^{-\frac{E}{kT}} - e^{-\frac{E}{kT}}(-\frac{E}{kT}) e^{-\frac{E}{kT}}}{(1 + e^{-\frac{E}{kT}})^2} \right\} \\ = \frac{E^2 e^{\frac{E}{kT}}}{(1 + e^{\frac{E}{kT}})^2}$$

- ⑦ For which gas the ratio of specific heat (C_p/C_V) will be largest (Jest 2014)

$$\Rightarrow \frac{C_p}{C_V} = \gamma = 1 + \frac{2}{f}$$

γ is large for monoatomic

Mono: $f = 3$

dia: $f = 5$

Tria: $f = 9$

hexa: $f = 18$

Ice of density ρ_1 melts at pressure P and absolute temperature T to form water of density ρ_2 . The latent heat of melting of 1 gm of ice is L . What is the change in the internal energy ΔU resulting from the melting of 1 gm of ice. (2014-JEST)

\Rightarrow From we have

$$\Delta Q = \Delta U + \Delta W \Rightarrow dQ = dU + PdV$$

$$\rho = \frac{m}{V}$$

$$dU = dQ - PdV$$

$$V = \frac{m}{\rho}$$

$$dU = mL + P \int \frac{d\rho}{\rho^2}$$

$$dV = -\frac{m}{\rho^2} d\rho$$

$$= L + P \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right)$$

\Rightarrow For a system in thermal eqbm with a heat bath at temperature T which is correct (Jest-2015)

$$Z = \sum e^{-\beta E_i}$$

$$\langle E \rangle = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$

$$\frac{\partial Z}{\partial \beta} = \sum -E_i e^{-\beta E_i}$$

$$\frac{\partial}{\partial \beta} \langle E \rangle = \frac{-\sum e^{-\beta E_i} E_i e^{-\beta E_i} + \sum E_i e^{-\beta E_i} E_i e^{-\beta E_i}}{(\sum e^{-\beta E_i})^2}$$

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$

$$= \frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} + \frac{\sum E_i^2 e^{-2\beta E_i}}{(\sum e^{-\beta E_i})^2}$$

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \langle E^2 \rangle$$

$$\frac{\partial}{\partial \beta} \langle E \rangle = \langle E \rangle^2 - \langle E^2 \rangle$$

\Rightarrow An ideal gas is compressed adiabatically from an initial volume V to final volume dV and a work w is done on the system is doing so. The final pressure of the gas (Jest 2015)

$$\Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma \quad w = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

$$P_1 V^\gamma = P_2 d^\gamma V^\gamma$$

$$w(1-\gamma) = P_2 dV - P_2 d^\gamma V$$

$$P_1 = P_2 d^\gamma$$

$$w(1-\gamma) = P_2 V (d - d^\gamma)$$

$$P_2 = \frac{w}{V} \frac{(1-\gamma)}{(d - d^\gamma)}$$

(22) A particle in thermal eqm has only 3 possible states with energies $-\epsilon, 0, \epsilon$. If a system is maintained at a temperature $T \gg \frac{\epsilon}{k_B}$, then the average energy (Jest 2015)

$$\Rightarrow \text{Partition function } Z = \sum e^{-\beta E} \\ = \frac{1}{1+e^{-\beta E}+e^{\beta E}}$$

$$\ln Z = \ln (1+e^{-\beta E}+e^{\beta E})$$

$$\langle U \rangle = -\frac{\partial}{\partial \beta} (\ln Z) = -\left[\frac{-\epsilon e^{-\beta E} + \epsilon e^{\beta E}}{1+e^{-\beta E}+e^{\beta E}} \right]$$

$$U = \left[\epsilon \left[\frac{e^{-\beta E} - e^{\beta E}}{1+e^{-\beta E}+e^{\beta E}} \right] \right] = \epsilon \left[\frac{(1-\beta E) - (1+\beta E)}{1+1-\beta E+1+\beta E} \right] = -\frac{2\epsilon^2}{3kT}$$

(23) The blackbody at a temperature 6000K emits a radiation whose intensity spectrum peaks at 600nm. If temperature is reduced to 300K, the spectrum will peak at (Jest 2015)

$$\lambda_m T = \text{Constant}$$

$$\lambda_{m_1} T_1 = \lambda_{m_2} T_2$$

$$6000 \times 600 = 300 \lambda_2$$

$$\lambda_2 = \frac{3600000}{300}$$

$$\lambda_2 = 12000 \text{ nm}$$

(24) Consider N classical Particle at temperature T, each of which can have two possible energies 0 and ϵ . The number of particle in the lower energy level (N_0) and higher energy level (N_ϵ) levels are related by (Jam 2020)

$$\Rightarrow \text{Partition function } Z = \sum e^{-\beta E} = (1+e^{-\beta E})$$

$$N_0 = \frac{N}{1+e^{-\beta E}} \quad N_\epsilon = \frac{N e^{-\beta E}}{1+e^{-\beta E}} = N_0 e^{-\beta E}$$

$$\frac{N_0}{N_\epsilon} = e^{\frac{E}{kT}}$$

- 2) One mole of an ideal gas having $\gamma = 1.6$ mixed with one mole of another ideal gas $\gamma = 1.4$ then C_p, C_V , for the mixture will be (Jest 2020)

$$\Rightarrow \gamma = 1 + \frac{2}{f_1} = 1.6 \quad 1 + \frac{2}{f_2} = 1.4$$

$$f_1 = 3.33 \quad f_2 = 5$$

$$C_{p1} = \left(1 + \frac{f_1}{2}\right)R = 2.665R$$

$$C_{V1} = 1.665R$$

$$C_{p2} = \left(1 + \frac{f_2}{2}\right)R = 3.5R$$

$$C_{V2} = 2.5R$$

$$C_{Vm} = \frac{n_1 C_{V1} + n_2 C_{V2}}{n_1 + n_2} = \frac{(1.665 + 2.5)R}{2} = 2.0825R$$

$$C_{Pm} = \frac{n_1 C_{p1} + n_2 C_{p2}}{n_1 + n_2} = \frac{(2.665 + 3.5)R}{2} = 3.0825R$$

$$C_{Pm} = 1.48 C_{Vm}$$

- 2) Consider two blackbody of radii R_1 and R_2 at temperature $T_1 = 1000K$ and $T_2 = 2000K$ respectively. They both emit radiation of power 1KW. The ratio of R_1/R_2 is (Jam 2020)

$$\Rightarrow \text{Power } P = \sigma A T^4 \Rightarrow A_1 T_1^4 = A_2 T_2^4$$

$$R_1^2 T_1^4 = R_2^2 T_2^4 \Rightarrow \frac{R_1}{R_2} = \frac{T_2^2}{T_1^2} = 4$$

- 2) A body at a temperature T is brought into contact with a reservoir at temperature $2T$. Thermal eqm is established at constant pressure. The total change in entropy of the body and reservoir in unit of C_p (Jam 2020)

$$\begin{aligned} \Delta S_1 &= m C_p \ln\left(\frac{T_2}{T_1}\right) & \Delta S_2 &= C_p \ln 2 - 0.5 C_p \\ &= m C_p \ln\left(\frac{2T}{T}\right) & &= (0.69 - 0.5) C_p \\ &= m C_p \ln 2 & &= 0.19 C_p \end{aligned}$$

$$\Delta S_2 = -m C_p \frac{(T_2 - T_1)}{T_2} = -m C_p \frac{T}{2T} = -\frac{1}{2} m C_p$$

⑤ The fermi-dirac distribution function
(Jan 2019)

$$\Rightarrow f(E) = \frac{1}{1 + e^{\left(\frac{E-E_F}{kT}\right)}}$$

⑥ In a heat engine based on the Carnot cycle, heat is added to working substance at constant Temperature (Jan 2019)

⑦ Isothermal Compressibility is given by

$$-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (\text{Jan 2019})$$

⑧ A red star having radius r_R at a temperature T_R and a white star having radius r_w at a temperature T_w , radiate the same power. If these stars radiate as perfect black bodies then (Jan 2019)

$$\Rightarrow P = \sigma A T^4 = \sigma \pi r^2 T^4$$

$$r_1^2 T_1^4 = r_2^2 T_2^4 \quad \frac{T_R}{T_w} = \sqrt{\frac{r_w}{r_R}} \quad r_R > r_w \\ T_w > T_R$$

$$r_R^2 T_R^4 = r_w^2 T_w^4$$

⑨ During free expansion of an ideal gas under adiabatic condition the internal energy —
(Jan 2019)

$$\Rightarrow dQ = dU + dW \quad \text{Adiabatic } dQ = 0 \\ dU = 0 \quad \text{free exp. } dW = 0$$

Internal energy remain same

⑩ For the thermodynamic system (Jan 2019)

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

Two gases having molecular diameters D_1 and D_2 and mean free path λ_1 and λ_2 if $D_2 = 2D_1$ then

$$\lambda_1/\lambda_2 \quad (\text{Jam 2019})$$

$$\Rightarrow \lambda = \frac{1}{\sqrt{2} \pi d^2 n} \Rightarrow \lambda \propto \frac{1}{d^2}$$

$$\Rightarrow \frac{\lambda_1}{\lambda_2} = \left(\frac{D_2}{D_1} \right)^2 = 4$$

A diatomic gas undergoes adiabatic expansion against the piston of a cylinder. As a result, the temperature of the gas drops from 1150K to 400K. The number of moles of gas required to obtain 2300J. of the work from expansion (Jam 2019)

$$\Rightarrow T_2 = 1150 \text{ K} \quad w = 2300 \quad \gamma = 7/5 = 1.4$$

$$T_1 = 400 \text{ K}$$

$$w = \frac{n R}{1-\gamma} \ln T \Rightarrow 2300 = \frac{8.314 \times n}{0.4} \times 750$$

$$\Rightarrow n = 0.147 \approx 0.15 \text{ mole}$$

Two boxes A and B contain an equal number of molecules of same gas. If volumes are V_A and V_B and λ_A and λ_B denote respective mean free path then (Jam 2018)

$$\Rightarrow n = \frac{N}{V} \quad n_A = \frac{N}{V_A} \quad n_B = \frac{N}{V_B} \quad \lambda = \frac{1}{\pi d^2 n}$$

$$\lambda \propto \frac{1}{n} \propto \frac{V}{N} \Rightarrow \frac{\lambda_A}{\lambda_B} = \frac{V_A}{V_B} \Rightarrow \frac{\lambda_A}{V_B} = \frac{\lambda_B}{V_B}$$

For 1 mole of a gas $pV = A(1 + \frac{B}{V})$. Volume changes from V_1 to V_2 . Find work done (Jam 2018)

$$\Rightarrow p = A \left(\frac{1}{V} + \frac{B}{V^2} \right) \quad w = \int p dV = A \int \frac{dV}{V} + AB \int \frac{dV}{V^2}$$

$$= A \lambda n \frac{V_2}{V_1} + AB \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

(3) A hot body with constant heat capacity 800 J/K at temperature 925 K is dropped gently into a vessel containing 1 kg of water at temperature 300 K and the combined system is allowed to reach eqm. The change in the total entropy ΔS is (Jam 2022)

\Rightarrow Let T_f be the final temperature

$$m_1 C_1 (T_1 - T_f) + m_2 C_2 (T_2 - T_f) = 0$$

$$800 (925 - T_f) + 4200 (300 - T_f) = 0$$

$$\cancel{5000 T_f} = 400 \times 5000 \Rightarrow T_f = 400 \text{ K}$$

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= m_1 C_1 \ln\left(\frac{T_f}{T_1}\right) + m_2 C_2 \ln\left(\frac{T_f}{T_2}\right)$$

$$= 800 \ln\left(\frac{400}{925}\right) + 4200 \ln\left(\frac{400}{300}\right)$$

$$= 1208.26 - 670 = 537.5 \text{ J/K}$$

(iv) A system undergoes a thermodynamic transformation from state S_1 to S_2 via two different paths 1 and 2. The heat absorbed and work done along path 1 are 50 J and 30 J , respectively. If the heat absorbed along path 2 is 30 J , the work done along path 2 is (Jam 2021)

$$\Rightarrow \Delta Q_1 = 50 \text{ J} \quad \Delta Q_1 = \Delta U + \Delta W_1$$

$$\text{and } \Delta Q_2 = 30 \text{ J} \quad 50 = \Delta U + 30 \Rightarrow \Delta U = 20 \text{ J}$$

$$\Delta W_2 = \Delta Q_2 - \Delta U$$

$$= 30 - 20 = 10 \text{ J}$$

- ③ The rms velocity of molecules of oxygen gas is given by v at some temperature T . The molecules of another gas have the same rms velocity at temperature $T/16$. The second gas is (Jam 2021)

$$\Rightarrow \text{rms velocity } V_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$\frac{(V_{\text{rms}})_{\text{O}_2}}{(V_{\text{rms}})_{\text{H}_2}} = \sqrt{\frac{T_{\text{O}_2}}{T_{\text{H}_2}} \cdot \frac{M_{\text{H}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{T}{T} \cdot \frac{1}{16}} = 1$$

The second gas is hydrogen

- ④ An ideal gas with adiabatic exponent γ undergoes a process in which its pressure P is related to its volume V by the relation $P = P_0 - \alpha V$. The volume starts from being very close to zero and increases monotonically to P_0/α . At what value of volume during the process does the gas have maximum entropy? (JEST 2016)

7)

In adiabatic process entropy

$$S = C_V \ln(PV^\gamma) + \text{constant}$$

$$= C_V \ln [(P_0 - \alpha V)V^\gamma] + \text{constant}$$

$$\frac{ds}{dv} = \frac{C_V}{(P_0 - \alpha v)V^\gamma} [-\alpha V^{\gamma-1} + (P_0 - \alpha v) \gamma V^{\gamma-1}] = 0$$

$$\alpha V^{\gamma-1} = (P_0 - \alpha v) \gamma V^{\gamma-1}$$

$$\frac{\alpha}{(P_0 - \alpha v)} = \gamma V^{-1}$$

$$V_{\max} = \frac{\gamma}{\alpha(\gamma+1)} P_0$$

(32) A gas of N molecules of mass m is confined in a cube of volume $V = L^3$ at temperature T . The box is in a uniform gravitational field $-g\hat{z}$. Assume that the potential energy of a molecule is $U = mgz$. ($z, 0, L$) is the vertical coordinate in the box. The Pressure is (Jest 2016)

=) The Partition function is given by

$$Z_N = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \left(\frac{KTN}{mgl} \right)^N \left[1 - \exp\left(-\frac{mgl}{kT}\right) \right]^N$$

$$F = -k_B T \ln Z_N \Rightarrow P = -\left(\frac{\partial F}{\partial V}\right) = \frac{KTN}{V}$$

(33) For a quantum mechanical harmonic oscillator with energies $E_n = (n + \frac{1}{2})\hbar\omega$. The Partition function is — (Jest 2016)

$$\Rightarrow Z = \sum e^{-\beta E_i} = e^{-\frac{\hbar\omega\beta}{2}} + e^{-\frac{3\hbar\omega\beta}{2}} + e^{-\frac{5\hbar\omega\beta}{2}} + e^{-\frac{7\hbar\omega\beta}{2}} + \dots \\ = \frac{e^{-\frac{\hbar\omega\beta}{2}}}{1 - e^{\frac{\hbar\omega\beta}{kT}}} = \frac{e^{\frac{\hbar\omega}{2kT}}}{e^{\frac{\hbar\omega}{kT}} - 1}$$

(34) In a thermodynamic process the volume of one mole of an ideal gas is varied as where $V = \alpha T^{-1}$ is constant. The adiabatic exponent of the gas γ . What is the amount of heat received by the gas if the temperature of the gas increases by ΔT in the process? (Jest 2018)

$$V = \frac{\alpha}{T} \quad W = \int P dV = \int \frac{RT}{V} dV = \int \frac{RT}{\alpha} \left(-\frac{\alpha}{T^2} \right) dT \\ dV = -\frac{\alpha}{T^2} dT$$

$$\Delta U = Q - \Delta T = \frac{R \Delta T}{\gamma - 1}$$

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

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 eqm at temperature T . The total energy $E(T, H)$ of the collection is (Jest 2018)

\Rightarrow Partition function $-\mu H, \mu H$ non degenerate
 0 is doubly degenerate

$$\begin{aligned} Z = \sum g_i e^{-\beta E_i} &= 2 + e^{-\beta \mu H} + e^{\beta \mu H} \\ &\approx 2 + 2 \left(\frac{e^{-\beta \mu H} + e^{\beta \mu H}}{2} \right) \\ &= 2 + 2 \cosh(\beta \mu H) \end{aligned}$$

$$Z_N = \left[2 + 2 \cosh\left(\frac{\mu H}{kT}\right) \right]^N \Rightarrow \chi_n Z_N = N \chi_n \left[2 + 2 \cosh(\mu H \beta) \right]$$

$$U = -\frac{\partial}{\partial \beta} (\chi_n Z) = -\frac{N \mu H \sinh\left(\frac{\mu H}{kT}\right)}{\left[1 + \cosh\left(\frac{\mu H}{kT}\right) \right]}$$

\Rightarrow Consider a system of N distinguishable particles with two energy levels for each particle: a ground state with energy zero and excited state with energy $\epsilon > 0$. What is the average energy per particle if $T \rightarrow \infty$ (Jest 2019)

\Rightarrow Partition function $Z = \sum g_i e^{-\beta E_i}$

$$= (1 + e^{-\beta \epsilon})$$

$$\chi_n Z = \chi_n (1 + e^{-\beta \epsilon})$$

$$\frac{\partial}{\partial \beta} (\chi_n Z) = -\frac{\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \Rightarrow \langle E \rangle = \frac{\epsilon}{e^{\beta \epsilon} + 1}$$

$$\beta \rightarrow 0 \quad \langle E \rangle \rightarrow \frac{\epsilon}{2}$$

(41) Consider a diatomic molecule with an infinite number of equally spaced non-degenerate energy levels. The spacing between any two adjacent levels is ϵ . and ground state energy is zero what is the single particle partition function Z (Jest 2019)

\Rightarrow Partition function $Z = \sum e^{-\beta E_i}$

$$Z = 1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon} + e^{-3\beta \epsilon} + \dots = \frac{1}{1 - e^{-\beta \epsilon}}$$

(42) Consider an ideal gas whose entropy is given by $S = \frac{n}{2} \left[\sigma + 5R \ln \frac{V}{n} + 2R \ln \frac{V}{n} \right]$. The specific heat at constant pressure (Jest 2020)

$$\Rightarrow dS = dU + PdV \quad \left(\frac{\partial S}{\partial U} \right) = \frac{1}{T}$$

$$TdS = dU + PdV$$

$$\frac{5nR}{2} \cdot \frac{n}{U} \cdot \frac{1}{n} = \frac{1}{T} \Rightarrow U = \frac{5}{2} nRT$$

$$C_V = \left(\frac{\partial U}{\partial T} \right) = \frac{5}{2} nR \Rightarrow C_P = \frac{7}{2} nR$$

(43) Consider a system of two particles at temperature $T \rightarrow \infty$. Each of them can occupy three different quantum energy levels having energies $0, \epsilon, 2\epsilon$ and both of them cannot occupy the same energy level. What is the average energy of the system? (Jest 2020)

\Rightarrow Partition function

$$Z = \sum e^{-\beta E_i} = e^{-\beta \epsilon} + e^{-3\beta \epsilon} + e^{-2\beta \epsilon}$$

$$\ln Z = \ln (e^{-\beta \epsilon} + e^{-3\beta \epsilon} + e^{-2\beta \epsilon})$$

$$\frac{\partial}{\partial \beta} (\ln Z) = - \left[\frac{\epsilon e^{-\beta \epsilon} + 3\epsilon e^{-3\beta \epsilon} + 2\epsilon e^{-2\beta \epsilon}}{e^{-\beta \epsilon} + e^{-3\beta \epsilon} + e^{-2\beta \epsilon}} \right]$$

$$\langle E \rangle = - \frac{\partial}{\partial \beta} (\ln Z) = \frac{6\epsilon}{3} = 2\epsilon \quad (T \rightarrow \infty)$$

0	ϵ	2ϵ	E
1	1		ϵ
	1	1	3ϵ
		1	2ϵ

(iv) Consider a system consisting of three non-degenerate energy levels with energies 0, ϵ and 2ϵ . In the limit of infinite temperature $T \rightarrow \infty$, the probability of finding a particle in the ground state (Jest 2021)

$$\Rightarrow \text{Partition function } Z = \sum e^{-\beta E_i} = (1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon})$$

$$\begin{aligned}\text{Probability } p &= \frac{1}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}} \quad \frac{1}{kT} \rightarrow 0 \\ &= \frac{1}{3}\end{aligned}$$

(v) M grams of water at temperature T_a is adiabatically mixed with an equal mass of water at temperature T_b , keeping the pressure constant. Find the change in entropy. Find the change in entropy (Jest 2021)

$$\Rightarrow \text{As. } \Delta Q = 0 = m c_p (T_a - T_f) + m c_p (T_b - T_f) = 0$$

$$\Rightarrow T_f = \left(\frac{T_a + T_b}{2} \right)$$

$$\Delta S_1 = m c_p \ln \left(\frac{T_f}{T_a} \right) = m c_p \ln \left[\frac{T_a + T_b}{2T_a} \right]$$

$$\Delta S_2 = m c_p \ln \left(\frac{T_f}{T_b} \right) = m c_p \ln \left[\frac{T_a + T_b}{2T_b} \right]$$

The change in entropy $\Delta S = \Delta S_1 + \Delta S_2$

$$= m c_p \left[\ln \frac{(T_a + T_b)^2}{4T_a T_b} \right]$$

$$= m c_p \left[\frac{(T_a - T_b)^2 + 4T_a T_b}{4T_a T_b} \right]$$

$$= m c_p \ln \left[1 + \frac{(T_a - T_b)^2}{4T_a T_b} \right]$$

(17) A cylinder contains 16 g of O₂. The work done when the gas is compressed to 75% of the original volume at constant temperature of 27°C is
 (Jam 2016)

=)

$$\text{No of mole, } n = \frac{w}{M} = \frac{16}{32} = 0.5 \text{ mole}$$

$$V_2 = 0.75 V_1 \quad T = 300\text{K}$$

$$w = nRT \ln \left(\frac{V_2}{V_1} \right) = 0.5 \times 8.314 \times 300 \ln (0.75) \\ = -358.76 \text{ J}$$

work done = 358.76 Joule

(18) V v/s T curves at constant pressure P₁ and P₂ for ideal gas shown in figure

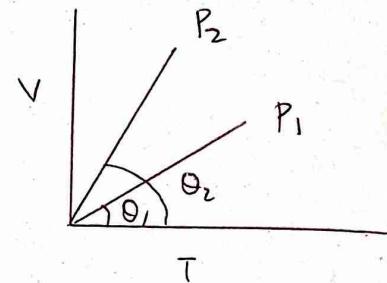
=)

$$PV = RT$$

$$\frac{V}{T} = \frac{R}{P} = \text{slope} = \tan \theta$$

$$\tan \theta \propto \frac{1}{P}$$

$$\tan \theta_2 > \tan \theta_1 \Rightarrow P_1 > P_2$$



(19)

For a diatomic ideal gas near room temperature what fraction of heat supplied is available for ext. work if the gas is expanded at constant pressure

$$\Rightarrow \frac{\Delta w}{\Delta q} = \frac{R \Delta T}{C_P \Delta T} = \frac{R}{\frac{7}{2} R} = \frac{2}{7} R \quad C_P = \left(\frac{f}{2} + 1\right) R \\ = \frac{7}{2} R$$

=)

Energy density $\frac{U}{V}$ of an ideal gas is related to the pressure p as

$$P = \frac{1}{3} M V^2 = \frac{1}{2} M V^2 \times \frac{3}{2} = \frac{3}{2} \frac{U}{V}$$

$$P V = \frac{2}{3} U$$

⑦ A system of N noninteracting classical point particles is constrained to move on the 2D surface of a sphere. The internal energy is

\Rightarrow Internal energy

$$\text{No of Particle} \times \text{degree of freedom} \times \frac{1}{2} kT$$

$$2N \frac{kT}{2} = Nk_B T$$

⑧ The isothermal Compressibility, K of an ideal gas at temp. T_0 and V_0 is

$$\Rightarrow \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

⑨ The mean value of $(V_x + V_y)^2$ is

$$\Rightarrow (V_x + V_y)^2 = V_x^2 + V_y^2 + 2V_x V_y$$

$$\begin{aligned} \langle (V_x + V_y)^2 \rangle &= \langle V_x^2 \rangle + \langle V_y^2 \rangle + 2\langle V_x \rangle \langle V_y \rangle \\ &= \frac{K_B T}{m} + \frac{K_B T}{m} + \frac{2K_B T}{m} \end{aligned}$$

⑩ For a gas under isothermal condition its pressure P . Varies with Volume V as $P \propto V^{-5/3}$. Bulk modulus B is proportional to

$$\Rightarrow P \propto V^{-5/3} \quad B = -V \left(\frac{\partial P}{\partial V} \right)$$

$$P = KV^{-5/3} \quad = \frac{5}{3} KV^{-5/3} \Rightarrow B \propto V^{-5/3}$$

$$\left(\frac{\partial P}{\partial V} \right) = -\frac{5}{3} KV^{-8/3}$$

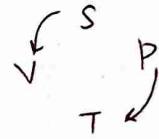
⑪ Temperature of mixture

$$T_{\text{mix}} = \frac{n_1 f_1 T_1 + n_2 f_2 T_2}{n_1 f_1 + n_2 f_2}$$

$$T_f = \frac{P_1 V_1 + P_2 V_2}{\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2}}$$

(2) The Vander Waal's eqn for 1 mole rd gas is given by $(P + \frac{a}{V^2})(V - b) = RT$. If U be the internal energy then $(\frac{\partial U}{\partial V})_T$ is

$$\Rightarrow dQ = dU + PdV$$



$$TdS = dU + PdV$$

$$T(\frac{\partial S}{\partial V}) = (\frac{\partial U}{\partial V}) + P$$

$$T(\frac{\partial P}{\partial T}) - P = (\frac{\partial U}{\partial V})_T$$

$$(P + \frac{a}{V^2}) = \frac{RT}{V-b} \Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

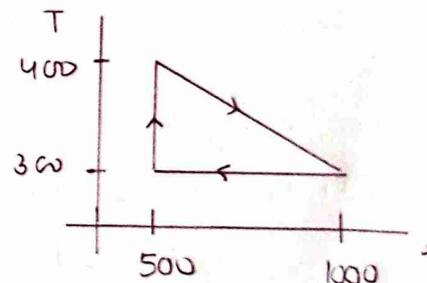
$$\Rightarrow (\frac{\partial P}{\partial T}) = \frac{R}{V-b}$$

$$\frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = (\frac{\partial U}{\partial V})_T \Rightarrow (\frac{\partial U}{\partial V})_T = \frac{a}{V^2}$$

(3) The efficiency of the enginee is

\Rightarrow work done

$$W = \frac{1}{2} \times (400 - 300) \times 500 \\ : 25,000 J$$



$$Q = 25,000 + (300 \times 500) = 175,000 J$$

$$\eta = \frac{W}{Q} = \frac{25,000}{175,000} = 14.3\%$$

(4) A steam turbine is operated with an intake temperature $400^\circ C$ and exhaust temperature $150^\circ C$ which of the following value of work the turbine may perform for a given heat input Q

$$T_1 = 400^\circ C = 673$$

$$\eta = 1 - \frac{T_2}{T_1} \cdot \frac{W}{Q}$$

$$T_2 = 150^\circ C = 433$$

$$W = 0.40 Q$$

⑥ Two thermally isolated identical systems have heat capacities which vary as $C_V = \beta T^3$. Initially, one system is at 300K and the other at 400K. The systems are then brought into thermal contact and the combined system is allowed to reach thermal equilibrium. The final temperature of combined system (JAM 2013)

⇒ change in internal energy

$$dU_1 = C_V dT = \beta T^3 dT$$

$$\Delta U_1 = \int dU_1 = \int_{300}^{400} \beta T^3 dT = \frac{\beta}{4} [T^4 - (300)^4]$$

$$\Delta U_2 = \int dU_2 = \int_T^{400} \beta T^3 dT = \frac{\beta}{4} [(400)^4 - T^4]$$

$$\therefore T^4 - (300)^4 = (400)^4 - T^4$$

$$2T^4 = (400)^4 + (300)^4 \Rightarrow T = 360\text{K}$$

⑥ If Pressure $P = a\rho + b\rho^2$ (ρ = no density).

The work done for ρ_0 to $2\rho_0$.

⇒ work done

$$\rho = \frac{N}{V}$$

$$\begin{aligned} W &= \int P dV = \int (a\rho + b\rho^2) dV = aN \int \frac{dV}{V} + bN^2 \int \frac{dV}{V^2} \\ &= aN \int_{N/\rho_0}^{N/2\rho_0} \frac{dV}{V} + bN^2 \int_{N/\rho_0}^{N/2\rho_0} \frac{dV}{V^2} = (aN \ln 2 + b \cdot \frac{N^2}{2}) \rho_0 V. \end{aligned}$$

⑦ The eqn of state of a gas $PV = \Theta$ - constant

The work done between the initial and final state V_i and V_f is proportional to

$$PV = \Theta$$

$$\begin{aligned} W &= \int P dV = \Theta \int \frac{dV}{V} = \Theta \ln \left(\frac{V_f}{V_i} \right) \\ &= \Theta \ln \left(\frac{V_f}{V_i} \right) \end{aligned}$$

(63)

A monoatomic gas is described by $p(V-nb) = nRT$.
 The maximum density in moles per unit volume
 to which the gas can be compressed

$$\Rightarrow p(V-nb) = nRT \quad \frac{df}{dp} = 0 = \frac{RT + Pb - Pb}{(RT + Pb)^2} = 0$$

$$PV = n(RT + Pb)$$

$$f = \frac{n}{V} = \frac{P}{RT + Pb}$$

$$f = \frac{P}{Pb} = \frac{1}{b}$$

(64)

An ideal gas at Pressure P is heated to twice its temp. Keeping its volume constant. It is then cooled its original temp at constant pressure. The work done is

$$\Rightarrow \text{At } 2P: T \rightarrow 2T \quad \Delta V = 0 \Rightarrow \Delta W = 0$$

$$\text{At } 2P: 2T \rightarrow T \quad V \rightarrow V_2 \Rightarrow W = 2P \times \frac{V}{2} = PV$$

(65)

In a thermally insulated container, 0.01 kg of ice at 273K is mixed with 0.1 kg of water at 300K. The change in entropy of the system is (GATE 2019)

$$\Rightarrow \text{Heat loss } \Delta Q = 0$$

$$mL + m_1 c_1 (T_i - T_f) + m_2 c_2 (T_i - T_f) = 0$$

$$(0.01 \times 4.2 \times 80) + 0.01 \times \frac{4.2}{2} (273 - T_f) + 0.1 \times 4.2 (300 - T_f) = 0$$

$$3.36 + 5.733 - 0.021 T_f + 12.6 - 0.42 T_f = 0$$

$$13.5093 = 0.441 T_f \Rightarrow T_f = 306.3 \text{ K}$$
