DIAS **Delhi Institute for Administrative Services**
India's Leading Institute for Civil Services Examination

ALL INDIA TEST SERIES CSE-2023

Candidate 's Information

Dias Roll No: 230001

1. NAME:- Aniket Hirde
2. UPSC ROLL NO:- 6701477
3. MOBILE NO:- ....
4. SUBJECT:- Thermodynamics TS-9
5. DATE:- 12-08-23

FOR OFFICE USE ONLY:-

Q.NO	MARKS
1.	32½
2.	22½
3.	30½
4.	
5.	26½
6.	33
7.	
8.	

TOTAL MARKS	145/250

EXAMINER SIGNATURE

INVIGILATOR SIGNATURE

18 Pusa Road Karol Bagh New Delhi-110005 Ph:01140079000, 9350934622 e-mail diasindia123@gmail.com

(Please do not write anything except the question number in this space) कृपया इस स्थान में प्रश्न संख्या के अतिरिक्त कुछ न लिखें।

उम्मीदवारों को इस हाशिए में नहीं लिखना चाहिए
Candidates must not write on this margin

Q1 (a)

Entropy is the measure of disorderliness in the system.

We know, $ds = \frac{dQ_{rev}}{T}$. Here $dQ = mC_p dT$

$\Rightarrow 5 \times 4.18 (T - 273) = 5 \times 4.18 (353 - T)$

$\Rightarrow 2T = 626 \Rightarrow \boxed{T = 313K}$

Where T = final temp. of water.

$\Rightarrow dS_1 = \int_{273}^{313} mC_p \frac{dT}{T} = 5 \times 4.18 \times \ln \frac{313}{273} = 2.85 \text{ kJ/k}$

$dS_2 = \int_{353}^{313} mC_p \frac{dT}{T} = 5 \times 4.18 \times \ln \frac{313}{353} = -2.51 \text{ kJ/k}.$

$\Rightarrow \text{Total } \Delta S = \Delta S_1 + \Delta S_2 = \boxed{0.336 \text{ kJ/k}}$

$6\frac{1}{2}/10$

∴ Total change in entropy of System is $\boxed{0.336 \text{ kJ/k}}$ i.e. $\Delta S > 0 \rightarrow$ consistent with law of constant entropy increase.

(1) (b)

Maxwell- Boltzmann gives the statistical distribution for distinguishable particles.

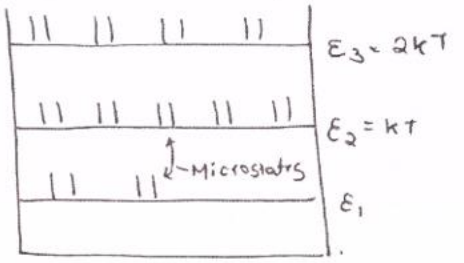


Fig 1. Macro-micro states

Given $T = 100K$,

$\Rightarrow kT = 1.38 \times 10^{-21} J$.

We know, $\frac{n_i}{g_i} = Ae^{-\varepsilon_i/kT}$

$\Rightarrow n_1 = 2A$; $n_2 = 5Ae^{-1}$

& $n_3 = 4Ae^{-2}$.

$\Rightarrow$ Total $N = \sum n_i = 2A + \frac{5A}{e} + \frac{4A}{e^2} = \underline{4.38A}$

$\Rightarrow P(\varepsilon_3) = \frac{n_3}{N} = \frac{4A}{e^2 \cdot 4.38} = \boxed{12.35\%}$.

$P(\varepsilon_1) = \frac{n_1}{N} = \frac{2A}{4.38A} = \boxed{45.6\%}$.

$\frac{6\frac{1}{2}}{10}$

This verifies the distribution that at lower temperature, most of the particles are in ground state.

Q1 (c).

Carnot engine is a reversible engine working between 2 reservoirs of heat.

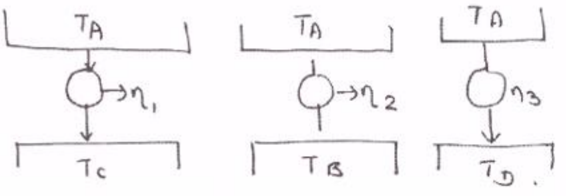


Fig 1. Carnot engine b/w reservoirs

We know,

$\eta_{rev} = 1 - \frac{T_2}{T_1}$

where T_2 = sink
T_1 - source temperature.

$\Rightarrow \eta_1 = 1 - \frac{T_C}{T_A}$; $\eta_2 = 1 - \frac{T_B}{T_A}$; $\eta_3 = 1 - \frac{T_D}{T_A}$

Given $\eta_1 = \frac{1}{2}(\eta_2 + \eta_3)$

$\Rightarrow 1 - \frac{T_C}{T_A} = \frac{1}{2} - \frac{T_B}{2A} + \frac{1}{2} - \frac{T_D}{2A}$.

$\Rightarrow \frac{T_C}{T_A} = \frac{1}{2}\frac{(T_B + T_D)}{T_A}$

$\Rightarrow \boxed{T_C = \frac{T_B + T_D}{2}}$

∴ Temperature of resorvoir C is mean of temperature of reservoirs B & D

6/10

Q1 (d)

Specific heat of material which varies with temperature ~~temperature~~ is measured at saturation.

> We know, $S_2 - S_1 = \frac{L}{T} \Rightarrow T\frac{dS_2}{dT} - \frac{TdS_1}{T} = \frac{dL}{dT} - \frac{L}{T}$

$\Rightarrow \frac{dL}{dT} - \frac{L}{T} = (C_2)_{sat} - (C_1)_{sat}$ where

$(C_2)_{sat}$ = sp. heat capacity of saturated vapor.

$(C_1)_{sat}$ = sp. heat capacity of saturated liquid.

Given: $L = 800 - 0.705T \Rightarrow \frac{dL}{dT} = -0.705$

At $T = 373\,K$, we have $\frac{L}{T} = \frac{800}{373} - 0.705 = 1.44$.

$\Rightarrow -0.705 - 1.44 = (C_2)_{sat} - (C_1)_{sat}$.

Assuming $(C_1)_{sat} = 1$ cal/g-k,

$$\boxed{(C_2)_{sat} = -1.14 \text{ cal/g-k}}$$

$6\frac{1}{2}$ / 10

As $(C_2)_{sat}$ is negative, net heat has to be extracted out of the system to increase heat while keeping vapour saturated.

Q1 (c)

Entropy is the measure of disorderliness in the system.

We know, $dS = \frac{dQ_{rev}}{T}$. For ideal gas,

$TdS = dQ = C_v dT + PdV$.

Also, $PV = RT$ for ideal gas

$\Rightarrow PdV + VdP = RdT$.

$\Rightarrow TdS = \frac{C_v}{R}[PdV + VdP] + PdV$.

$\Rightarrow TdS = C_p \frac{PdV}{R} + C_v \frac{VdP}{R}$

$\Rightarrow \cancel{T}dS = C_p \frac{dV}{V} + C_v \frac{dP}{P}$

$\Rightarrow \Delta S = \int_{V_1}^{V_2} C_p \frac{dV}{V} + \int_{P_1}^{P_2} C_v \frac{dP}{P}$

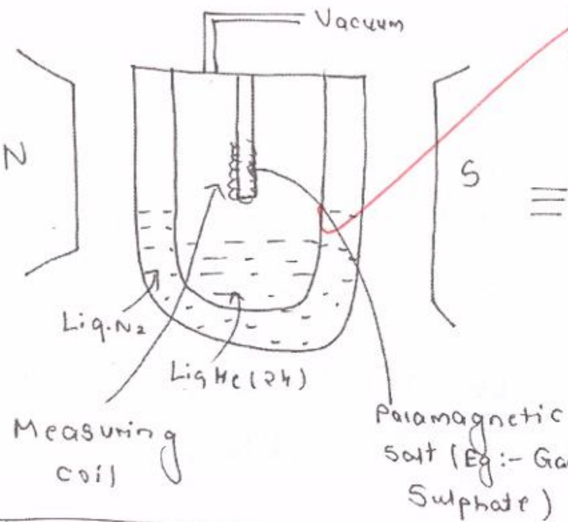
6½/10

$\Rightarrow \boxed{\Delta S = C_p \ln \frac{V_2}{V_1} + C_v \ln \frac{P_2}{P_1}}$

Entropy can be further used to check feasibility of a reaction

Q.2 (a)

Adiabatic demagnetization is a method of producing near zero temperatures (~0.0025k) by isothermal magnetization – adiabatic demagnetization repeatitvely of paramagnetic salt.



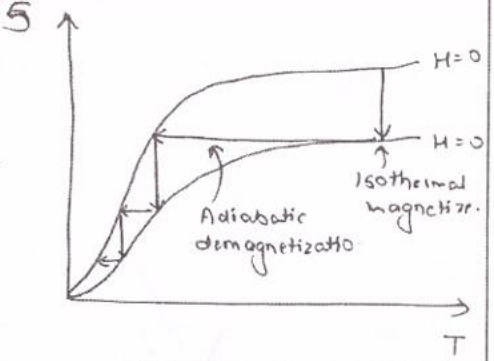


Fig 1. Experiment setup

Fig 2. S v/s T graph

Producing low temperatures :-

> Rock salt taken ⇒ PdV = 0

> Isothermally magnetized ⇒ Dipoles aligned along magnetic field. Any excess heat is taken out by vaccum pump.

> Adiabatically demagnetized ⇒ Dipoles re-align at cost of internal energy

$\Rightarrow$ temperature of sample drops.

> The TdS equation for paramagnetic salt is

$-TdS = C_H dT - \frac{CH}{T} dH$ $\Big\}$ C_H = sp. heat capacity.
C = Curie's constant

During adiabatic demagnetization, $dS = 0$.

$\Rightarrow C_H dT = \frac{CH}{T} dH \Rightarrow \int_{T_1}^{T_2} dT\,(T) = \int_{H}^{0} \frac{C}{C_H} H\,dH$

$\Rightarrow (T_2^2 - T_1^2) = \frac{CH^2}{C_H}$ $\Big\}$ Let $T_2 - T_1 = \Delta T$,
$T_1 + T_2 = 2T_{avg}$.

$\Rightarrow \boxed{\Delta T = \frac{CH^2}{2 C_H T_{avg}}}$

> Given, C_H (for 0.1 gm) = 1×10^{-3} Cal/k

$\Rightarrow \Delta T = \frac{0.05\,(10^8)}{2 \times 10^{-3} \times 3} \times 10^{-7} \times 0.1$ $\Big\}$ As $C = \text{erg}\,k\,g^{-1}\,\text{Oe}^{-2}$ in CGS.

$\Rightarrow \boxed{\Delta T = 1.99\,k}$ Here C_H considered in Joules.

As can be seen, the drop is significant due to pre-cooling at 3k.

Applications of adiabatic demagnetization

① In cryogencis of rockets

② Producing super-conductors.

However, scalability, pre-cooling remain the limitations

13/20

Q2 (b).

Carnot engine is a reversible engine of 2 isothermal, 2 adiabatic process operating between 2 temperatures.

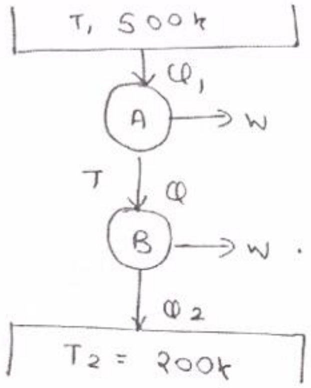


Fig 1. Canot engine in series

> We know, For Carnot engine,

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1} = \frac{W}{Q_1}$$

where Q_1 = heat absorbed.
Q_2 = heat rejected.
T_2 = sink temperature
T_1 = source temperature.

$$\Rightarrow 1 - \frac{T}{500} = \frac{W}{Q_1} = 1 - \frac{Q}{Q_1} \quad - ①$$

$$1 - \frac{200}{T} = \frac{W}{(Q/2)} = 1 - \frac{Q_2}{(Q/2)} \quad - ②$$

From eq. ①, $\frac{Q}{Q_1} = \frac{T}{500}$ — ③

Also, $\left(1 - \frac{T}{500}\right) Q_1 = \left(1 - \frac{200}{T}\right) \frac{Q}{2} = W$.

$$\Rightarrow \left(1 - \frac{T}{500}\right) = \left(1 - \frac{200}{T}\right) \frac{1}{2} \left(\frac{T}{500}\right) \quad \Big\} \text{ From eq. ③}$$

$\Rightarrow 1 - \frac{T}{500} = \frac{T}{1000} - \frac{1}{5}$

$\Rightarrow \frac{4}{5} = \frac{3T}{1000} \Rightarrow \boxed{T = 266.674}$

$\therefore$ The first engine rejects heat at $\boxed{266.674}$.

Carnot engine is the engine with maximum efficiency operating between two temperatures

02 / 15

Q 2 (c)

Maxwell's equations gives the relation between pressure, temperature, entropy, volume.

We know $\frac{\partial P}{\partial T}$ = Pressure coeff. of expansion.

$\Rightarrow \dfrac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial T}\right)_S}$ ✓

As P, T, S are state functions, $f(P,T,S) = 0$.

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial P}{\partial S}\right)_T \quad - ①$$

Show!

We know, $C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$ ✓ $- ②$

Substituting values from eq. ① & ②,

$$\frac{(C_p - C_v)}{T\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{-\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P}$$

We know, $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_p$.

From Maxwell's equations, $\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$

$\Rightarrow \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{-\partial p}{\partial s}\right)_T = 1$

→ Given equation becomes :-

$$\frac{C_p - C_v}{C_p} = 1 - \frac{C_v}{C_p} = \boxed{1 - \frac{1}{\gamma}}$$

$\frac{7\frac{1}{2}}{15}$

Hence, ratio of pressure coefficient of expansion at constant volume to constant entropy is $\underline{1 - 1/\gamma}$

Q 3 (a)

Diesel engine is a 4-stroke, 3 valve engine operating with diesel as a fuel.

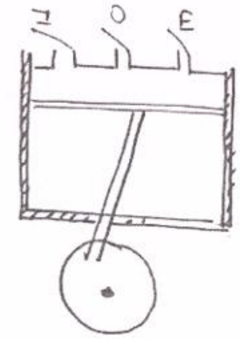


Fig 1. Diesel engine

≡ .

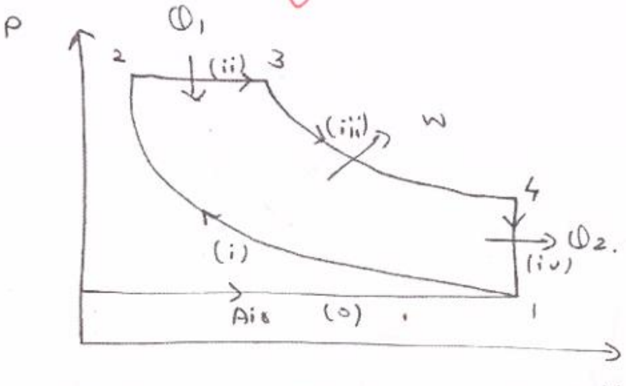


Fig 2. PV diagram of diesel engine

Working

- Air sucked in at constant pressure (0).
- Stroke - I :- Adiabatic compression

  Air compressed from volume v_1 to v_2, piston moves up — Air heated up ; $\rho_c = v_1/v_2$
- Stroke - II :- Isobaric heat addition

  Diesel sprinkled in heated air - burns
- Stroke - III :- Adiabatic work

  Piston pushed down, volume expands from v_3 to v_4 ; $\rho_e = \frac{v_4}{v_3}$

> Stroke -IV :- Isochoric heat rejection

Exhaust valve opened up, heat allowed to escape.

Efficiency $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)}$

As process (i) & (iii) are adiabats,

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$ & $P_3V_3^{\gamma} = P_4V_4^{\gamma}$

$\Rightarrow T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ & $T_3V_3^{\gamma-1} = T_4V_4^{\gamma-1}$

Assuming air ideal gas.

Writing all temperatures in terms of T_3,

$T_4 = T_3\left(\frac{1}{\rho_e}\right)^{\gamma-1}$ — ①.

Also, $V_1 = V_4 \Rightarrow \frac{T_3}{T_4}V_3^{\gamma-1} = \frac{T_2}{T_1}\cdot\left(\frac{V_2}{\cancel{V_1}}\right)^{\gamma-1}$

$\Rightarrow T_2 = \frac{T_3}{T_4}\cdot T_1\left(\frac{V_3}{V_2}\right)^{\gamma-1}$ $\cancel{\&}$ $\cancel{T}$.

$$\Rightarrow \cancel{\eta = 1 - \frac{1}{\gamma}\frac{\left[(T_3)\left(\frac{1}{\rho_e}\right)^{\gamma-1} - T_1\right]}{T_3 - T_2}}.$$

Also, $\frac{T_1V_1^{\gamma-1}}{T_4V_4^{\gamma-1}} = \frac{T_2V_2^{\gamma-1}}{T_3V_3^{\gamma-1}} \Rightarrow \frac{T_1}{T_4} = \frac{T_2}{T_3}\left(\frac{V_2}{V_3}\right)^{\gamma-1}$

as $V_1 = V_4$

$$\eta = 1 - \frac{1}{\gamma}\,\frac{T_4\left[1 - \frac{T_1}{T_4}\right]}{T_3\left[1 - \frac{T_2}{T_3}\right]} = 1 - \frac{1}{\gamma}\,\frac{\frac{T_4}{T_3}\left[1 - \left(\frac{V_2}{V_3}\right)^{\gamma-1}\frac{T_2}{T_3}\right]}{\left(1 - \frac{T_2}{T_3}\right)}$$

Now, $\frac{T_4}{T_3} = \left(\frac{1}{\rho_e}\right)^{\gamma-1}$; $\frac{V_2}{V_3} = \frac{\rho_e}{\rho_c}$.

Substituting, we get,

$$\boxed{\eta = 1 - \frac{1}{\gamma}\,\frac{\left[\left(\frac{1}{\rho_e}\right)^{\gamma} - \left(\frac{1}{\rho_c}\right)^{\gamma}\right]}{\left(\frac{1}{\rho_e}\right) - \left(\frac{1}{\rho_c}\right)}}$$

For carnot engine, $\eta = 1 - \frac{T_{min}}{T_{max}} = 1 - \frac{T_1}{T_3}$.

$$\eta_{diesel} = 1 - \frac{1}{\gamma}\,\frac{[T_1]\left[\frac{T_4}{T_1} - 1\right]}{T_3\left[T - \frac{T_2}{T_3}\right]}$$

Now as $\frac{T_4}{T_1} > 1$ & $\frac{T_2}{T_3} < 1$, $\left(\frac{\frac{T_4}{T_1} - 1}{1 - \frac{T_2}{T_3}}\right) > 1$.

$\Rightarrow 1 - \left(\frac{T_1}{T_3}\right)(A)\left(\frac{1}{\gamma}\right) = \eta_{diesel}$ as (A) is > 1,

$1 - \frac{T_1}{T_3}(A) < 1 - \frac{T_1}{T_3} \Rightarrow \boxed{\eta_{diesel} < \eta_{carnot}}$

13/20

Typically $\rho_e \approx 5$; $\rho_c \approx 17$

by design $\Rightarrow$ η_{diesel} is $\sim 56\%$. for

cars

Q3 (b)

Maxwell's relations are thermodynamic relations which relate P, S, T, V

> We have to find $\frac{\Delta Q}{\Delta P}$ } as pressure is increased on water.

$\Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T$ ✓ We know from Maxwell's relations,

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

$\Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$ ✓ } We know, $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}$

$\Rightarrow \Delta Q = -T\alpha(V)\Delta P$. ✓

8/15

Volume of 10 gm water = $10\,cc^3 = 10\times10^{-6}\,m^3$.

$\Rightarrow \Delta Q = -273(-6.7\times10^{-5})(10\times10^{-6})(1000\times10^{5})$

$\Rightarrow \boxed{\Delta Q = 18.29\,J}$ $= 1.829\,J$

As ΔQ is positive, heat is absorbed by the system & is equal to $\boxed{18.3\,J}$. ✓

Q.3 (c)

Clausius Clapeyron equation gives variation of boiling point with pressure.

We know, $\left(\frac{\partial P}{\partial T}\right) = \frac{L}{T(v_2 - v_1)}$ $\Bigg\}$ L = latent heat, v = specific volume, T = boiling point

Assuming for vapour stage, $v_2 >> v_1$,

$\frac{\partial P}{\partial T} = \frac{L}{T v_2}$ $\Bigg\}$ Assuming vapour behaves like ideal gas,

$\frac{\partial P}{\partial T} = \frac{L}{T\left(\frac{RT}{P}\right)} \Rightarrow \frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2}$

$\Rightarrow \int_{P_1}^{P_2} \frac{dP}{P} = \frac{L}{R}\int_{T_1}^{T_2} \frac{dT}{T^2}. \Rightarrow \underline{\ln\frac{P_2}{P_1} = \frac{-L}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$

Here P_2 = 1mm Hg $\qquad T_2$ = 1.2K
P_1 = 760mmHg (atm). $\qquad T_1$ = 4.2K.

$\Rightarrow \ln\left(\frac{1}{760}\right) = -\frac{L}{R}\left[\frac{1}{1.2} - \frac{1}{4.2}\right]$

$\Rightarrow L = 11.14R \Rightarrow \boxed{L = 92.65 \text{ J/mol-K}}$.

7½

This phenomenon is used in pressure cooker where pressure is increased to increase boiling point of water.

Q.5
(a)

Mean free path (λ) is the average distance traveled by molecule before it encounters another molecule

> Coefficient of viscosity (η) = Force per unit area per unit velocity gradient.

We know, $\eta = \frac{1}{3} \rho \bar{v} \lambda$.

where $\bar{v}$ = average velocity = $\sqrt{\frac{8kT}{\pi m}}$ } Assuming Maxwell Boltzman statistics.

At NTP, T = 20°c = 293K, $m_{(N_2)}$ = 28 amu.

$\Rightarrow \bar{v} = 469\ m/sec$

$\Rightarrow \lambda = \frac{3 \times 1.7 \times \cancel{10^{-4}}}{1.2} \times \frac{10^{-3}}{\cancel{10^{-4}}} \times \frac{1}{469}$.

$\Rightarrow \lambda = 9.05 \times 10^{-6}\ m$.

$\frac{6\frac{1}{2}}{10}$

$\therefore$ Mean free path of N_2 molecule is $\boxed{9.05\ \mu m}$. This can be further used to estimate radius of nitrogen.

Q5 (b).

Hydrogen at NTP can be considered as set of indistinguishable particles i.e. it follows Maxwell Boltzmann statistics.

We know, $n(\epsilon)(d\epsilon) = Ae^{-\epsilon/kT} \cdot g(\epsilon)\, d\epsilon$

where $g(\epsilon) = \frac{2\pi V}{h^3}(2m)^{3/2} \cdot \epsilon^{1/2}$,

$A = \frac{N}{Z}$ where $Z = \frac{V}{h^3}(2\pi mkT)^{3/2}$ $\Big\}$ Partition function.

$\Rightarrow n(\epsilon) = \frac{2N}{\sqrt{\pi}(kT)^{3/2}} \cdot \epsilon^{1/2} \cdot e^{-\epsilon/kT}\, d\epsilon$

At NTP, $T = 293\,K$; assuming $\epsilon = 0.02355\,eV$,

$n(\epsilon) = \frac{2N}{\sqrt{\pi}(2.5\times10^{-31})} \times (6.14\times10^{-11}) \times (0.394) \times 1.6\times10^{-23}$

$\Rightarrow \frac{n(\epsilon)}{N} = 1.75\times10^{-3}$

At NTP, 22.4 litres has Na no. of molecules

$\Rightarrow N$ for litre $= \frac{Na}{22.4}$

$\Rightarrow \boxed{n(\epsilon) = 4.69\times10^{19}}$

$\therefore \boxed{\sim 4.7\times10^{19}}$ molecules would be between the given energy range.

6/10

Q5 (c)

Maxwell - Boltzmann statistics gives the distribution for distinguishable particles

$$\frac{n_i}{g_i} = f(\epsilon_i) = Ae^{-\epsilon_i/kT}$$

n_i = # particles
g_i = density of states = 1 assumed here.

Energy levels are $-2kT, 0, 2kT$

$\Rightarrow n_1 = Ae^2 \; ; \; n_2 = A \; ; \; n_3 = A/e^2$.

$\Rightarrow$ Total no. of particles = $N = \sum n_i = A\left[e^2 + 1 + \frac{1}{e^2}\right]$
$= \underline{\underline{8.52A}}$.

Probability of finding the system in $\epsilon = 0$ state $P(\epsilon_2) = \frac{n_2}{N}$.

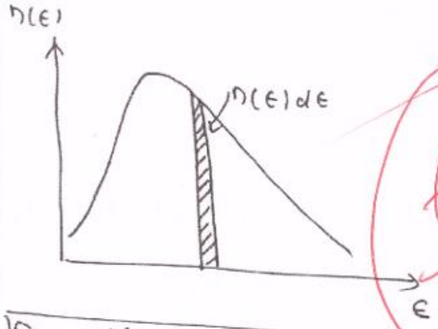


Fig 1. Maxwell Boltzmann distribution

$\Rightarrow P(\epsilon_2) = \frac{A}{8.52A} = 0.117$

6½/10

$\therefore$ Probability of finding particle in $\epsilon = 0$ state is $\boxed{11.7\%}$.

This is consistent with theory that larger no. of particles occupy lower levels.

Q5 (d)

Maxwell - Boltzmann, Bose - Einstein, Fermi - Dirac are three statistics which give distribution of distinguishable particles, bosons (Full integral spins & fermions (half-integral spin) respectively.

① Maxwell - Boltzmann.

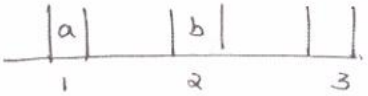


Fig 1. 3 states, 2 particles

ways in which particle can occupy same state = 3

Total no. of ways = $3^2 = 9$

$\Rightarrow$ # ways in which particles occupy different state = $9 - 3 = 6$.

$$\Rightarrow \frac{P(\text{same state})}{P(\text{diff. state})} = \frac{3}{6} = \boxed{\frac{1}{2}}.$$

② Bose - Einstein :

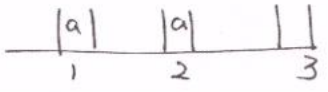


Fig 2. BE distribution

Particles are indistinguishable

$\Rightarrow$ Total no. of ways

$= {}^{g_i+n_i-1}C_{n_i} = {}^4C_2 = 6$

Total no. of ways to occupy same state = 3

$$\Rightarrow \frac{P(\text{same state})}{P(\text{diff. state})} = \frac{3}{3} = \boxed{1}.$$

③ <u>Fermi- Dirac:-</u> Fermions are half - spin particles by virtue of which they follow <u>Pauli's exculsion principle</u> ⇒ No two <u>particles</u> can have same state

$$\Rightarrow \frac{P_{(\text{same state})}}{P_{(\text{diff. state})}} = \boxed{0}.$$

7/10

Q5 (c).

Latent heat is the heat which is absorbed by a body at constant temperature when it changes phases.

We know, from Clausius Clapeyron equation,

$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$

$L = T(V_2 - V_1)\left(\frac{dP}{dT}\right)$

$S_2 - S_1 = \frac{L}{T}$ — ①

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

$\Rightarrow \frac{dL}{dT} - \frac{L}{T} = (C_2)_{sat} - (C_1)_{sat}$. So latent heat can become 0 in 2 cases.

L can be zero when either $V_2 - V_1 = 0$ or $\left(\frac{dP}{dT}\right) = 0$ occurs at CRITICAL POINT

① when $\Delta S = 0$ i.e. phase change occurs at constant entropy. We know $\left(\frac{\partial G}{\partial T}\right)_P \Rightarrow -S$

$\Rightarrow$ If $S = 0$, $\left(\frac{\partial G}{\partial T}\right) = 0 \Rightarrow$ This will happen for order of $\boxed{\text{transition} > 1}$

② when specific heat of saturated vapour = Specific heat of saturated liquid & dL/dT variation is small $\Rightarrow L \approx 0$

In such cases, liquid will immediately turn into vapour as it reaches boiling point.

Q6 (a). Real gases are the gases which deviate from ideal gas giving different eq. of state like $P(V-b) = RT$.

(i) We know, $dQ = dU + PdV$ — 1st law of thermodynamics.

Now, $dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$. But in this gas, there is no intermolecular interaction as a (vanderwall constant) $= 0$ $\Rightarrow \frac{\partial U}{\partial V} = 0$ $= T\left(\frac{\partial S}{\partial V}\right)_T - P$

Show $= T\left(\frac{\partial P}{\partial T}\right)_T - P$
$= \frac{RT}{V-b} - P = 0$

$\Rightarrow dU = C_V dT$.

$\Rightarrow dQ = C_V dT + PdV$. } As process is isothermal, $dT = 0$.

04

$dW = PdV = \frac{RT}{(V-b)} dV \Rightarrow \Delta W = RT \int_{V_1}^{V_2} \frac{dV}{(V-b)}$

$\Rightarrow \Delta W = \Delta Q = \boxed{RT \ln\left(\frac{V_2 - b}{V_1 - b}\right)}$

V_2 = expanded volume,
V_1 = initial volume.

(ii) In adiabatic expansion,

$dQ = 0$ & $PV^{\gamma} = \text{constant} \Rightarrow$ Here $P(V-b)^{\gamma} = k$

$\Rightarrow dW = PdV = \frac{k}{(V-b)^{\gamma}} dV \Rightarrow \Delta W = \int_{V_1}^{V_2} \frac{k}{(V-b)^{\gamma}} dV$

$\Rightarrow \Delta W = \frac{k}{1-\gamma}\left[\frac{V_2}{V_2^{\gamma}} - \frac{V_1}{V_1^{\gamma}}\right] = \frac{1}{(\gamma-1)}\left(P_1(V_1-b) - P_2(V_2-b)\right)$

04

⇒ For adiabatic, $\boxed{\Delta Q = 0}$

& $$\boxed{\Delta W = \frac{1}{\gamma - 1}\left[P_1(v_1-b) - P_2(v_2-b)\right]}$$

(iii) Isothermal expansion

$$\Delta W = RT\ln\left(\frac{v_2-b}{v_1-b}\right) = RT\ln\left(\frac{20.02-0.02}{0.2-0.02}\right)$$

⇒ $\Delta W = 4.71\,RT = \underline{7833.1\ J}$

In isothermal, $\Delta U = 0$, $\Delta Q = \Delta W$.

⇒ $\boxed{\Delta U = 0,\ \Delta Q = \Delta W = 7.83\ kJ}$

Adiabatic expansion

$\Delta W = \frac{R(T_1 - T_2)}{\gamma - 1}$ } where $T_1 = 200\ K$.
Now, we know, $P(v-b)^{\gamma} = K$

?

⇒ $T(v-b)^{\gamma-1} = \text{constant}$

⇒ $T_1(v_1-b)^{\gamma-1} = T_2(v_2-b)^{\gamma-1}$

⇒ $200(0.2-0.02)^{2/3} = T_2(20.02-0.02)^{2/3}$

⇒ $\underline{T_2 = 8.65\ K}$.

$$\Rightarrow \Delta W = \frac{R(200-8.65)}{5/3-1} = \underline{2386.5\,J}.$$

3

In adiabatic, $\Delta Q = 0$, $\Rightarrow \Delta U = -\Delta W$.

$$\therefore \boxed{\Delta U = -2.38\,kJ, \ \Delta Q = 0, \ \Delta W = 2.38\,kJ}$$

Isothermal process is ideal input process whereas, adiabatic process is ideal output process.

14/20

Q.6 (b)

Joule - kelvin coefficient in the relative drop in temperature with drop in pressure when a real gas is throttled through a porous plug.

$\therefore \mu$ = Joule kelvin coefficient $= \left(\frac{\partial T}{\partial P}\right)_H$ } As throttling is isoenthalpic.

Let $H(P,T) \Rightarrow dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$.

As $dH = 0$, & $\left(\frac{\partial H}{\partial T}\right)_P = C_P$ & $\partial H = \partial U + \overset{\partial(PV)}{\cancel{PdV}}$.

$\Rightarrow 0 = \frac{\partial}{\partial P}(U + PV)\, dP + C_P\, dT$.

$\Rightarrow \mu = \left(\frac{\partial T}{\partial P}\right) = -\frac{1}{C_P}\left[\frac{\partial U}{\partial P} + \frac{\partial}{\partial P}(PV)\right]$

> For Joule's law, $\frac{\partial U}{\partial P} = 0$ as there is no intermolecular interaction. But for real gases, $\partial U/\partial P \neq 0 \Rightarrow$ Deviates from Joule's law.

> Boyle's law is $\frac{\partial}{\partial P}(PV) = 0$. Hence we get $PV = RT$ for ideal gas. But for

real gas, $\frac{\partial}{\partial P}(PV) \neq 0 \Rightarrow$ Deviation from Boyle's law.

The first term $\left(\frac{\partial U}{\partial P}\right)$ always produces cooling while $\frac{\partial}{\partial P}(PV)$ can produce both cooling/heating.

Case of H_2 & He

> Assuming H_2, He following Vander Waals eq.,
$\left(P + a/v^2\right)(v-b) = RT$; we get $\mu = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$

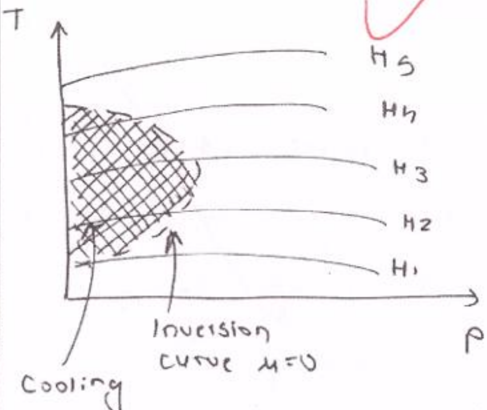


Fig 1. T v/s P for iso enthalpic process

We define inversion temp. as $T_i = \frac{2a}{Rb}$. If $T < T_i$, only then $\mu > 0 \Rightarrow$ cooling occurs.

But for He, $T_i = -240°C$

& For H_2, $T_i = -80°C$.

As normally $T > T_i$,

H_2 & He heat in Joule-kelvin expansion

$\frac{9.5}{15}$

This process is used to liquify gases in petrochemical industries via Linde's technique.

Q. 6 (c).

Specific heat is the heat required to increase temperature of unit mass of substance by 1 unit. Einstein & Debye gave two theories for specific heat :-

	Debye	Einstein
Cv	$C_v = 9R\left[4\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{e^x-1} - \frac{\theta_D}{T}\frac{1}{e^{\theta_D/T}-1}\right]$ θ_D = Debye temp.	$C_v = 3R\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}$ where θ_E = Einstein temp
Assumptions	① Molecules behave like Planck oscillator vibrating with different frequencies $[\nu_1 \nu_2 \dots \nu_m]$	① Molecules vibrate as planck oscillator, all with same frequency ν.
	② No concept of individual degree of freedom, Total # modes = 3N	② Each molecule has 3 degree of freedom
	③ Vibration is elastic i.e. has both transverse & longitudinal component	③ No such concept.

Limitations	① Valid only for isotropic solids	① Cannot explain $c_v \propto T^3$ at low temperature. ② No explaination for semi emperical curve fitting method to find θ_E.

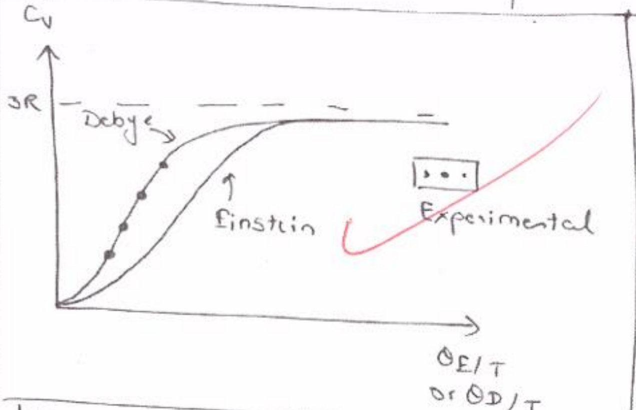


Fig 1. Cv v/s temperature

Given :-

$$U = \frac{9Nh}{\nu_m^3}\int_0^{\nu_m}\frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$$

Let $\frac{h\nu_m}{k} = \theta_D$

& $\frac{h\nu}{kT} = x$

$\Rightarrow$ x varies from 0 to θ_D/T.

9½/15

$$\Rightarrow U = \frac{9Nh}{\nu_m^3}\cdot\left(\frac{kT}{h}\right)^3\int_0^{\theta_D/T}\frac{x^2 dx}{e^x - 1}$$

$$\Rightarrow U = 9Nh\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^2 dx}{e^x-1}$$

} Using Lebinitz rule, $C_v = \frac{\partial U}{\partial T}$)

$$C_v = 9Nh\left[3\left(\frac{T^2}{\theta_D^3}\right)\int_0^{\theta_D/T}\frac{x^2dx}{e^x-1} + \frac{\left(\frac{T}{\theta_D}\right)^3\cdot\left(\frac{-\theta_D}{T^2}\right)\left(\frac{\theta_D}{T}\right)^2}{\left(e^{\theta_D/T}-1\right)}\right.$$

$$\Rightarrow \boxed{C_v = 9Nh\left[3\left(\frac{T^2}{\theta_D^3}\right)\int_0^{\theta_D/T}\frac{x^2dx}{e^x-1} - \frac{1}{e^{\theta_D/T}-1}\right]}$$

At low temp. this will show $\boxed{C_v \propto T^2}$.