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

CIVIL SERVICES EXAMINATION (MAINS) 2020
DIAS PHYSICS OPTIONAL TEST SERIES
Test VIII: Thermal & Statistical Physics

Time Allowed: 3 Hours **Max Marks: 250**

All Questions are compulsory .

Q1. (a) The melting point of lead under normal process is $600\ K$. What will be the change in its value when pressure is increased to 100 atmosphere. The density of lead in solid and liquid phases is $11.01\ gm/cm^3$ and $10.65\ gm/cm^3$ respectively. Latent heat of fusion is 24.5×10^7 erge/gm.

(b) Calculate the variation of C_p with pressure at constant temperature for a substance for which the equation of state is given by $V = \frac{RT}{p} - \frac{C}{T^3}$

(c) An electric current of 10 A is maintained for 1 sec. in a resistor of 250Ω while the temperature of the resistor is kept constant at 27^0C.

(i) What is the entropy change of the resistor ?

(ii) What is the entropy change of the universe ?

(d) Calculate Van der Waal's constants (i) a and b (ii) diameter of a molecule of Helium. Given $T_c = 5.3\ K$ $P_c = 2.25$ atoms and $R = 8.31 J/mole/{}^0K$.

(e) The coefficient of viscosity of oxygen at 15^0C is $196\ \mu$ poise. Calculate the diameter of a molecule of this gas. (Given $R = 8.4\ J/mole/{}^0K$ and mole atoms of oxygen is 32 a.m.u.) (10 X 5 = 50 MARKS)

Q2. (a) What is adiabatic demagnetization cycle? How do you achieve very low temperatures by this method? Derive an expression for fall of temperature and show that more cooling is produced when temperature is low .

(b) Show that entropy is a path independent function. Find out the expressions for change in entropy of 1 gm mole of an ideal gas in terms of (i) $P \& V$ (ii) $P \& T$ (iii) $T \& V$.

(c) The mean free path of the molecules of a gas is 2×10^{-7} m. Calculate the probability that a molecule will travel 6×10^{-7} m without making a collision, if temperature is doubled .

(20+15+15=50 marks)

Q3. (a) Show that Joule-Kelvin coefficient shows departure from Joules' and Boyle's laws. Hence analyse the result of porous plug experiment.

(b) For a Van der Waal's gas, derive the equation of the adiabatic curve in terms of the variable T and V.

(c) what is a Diesal cycle? Derive an expression for efficiency of a Diesal engine and show that it is less than a reversible Carnot engine .

(d) Under what conditions quantum statistical distributions converge to Maxwell-Bolzimann's statistics? Fix up the value of constant "μ" in Bose-Einstein distribution.

(15+10+15+10= 50 marks)

Q4. (a) Derive an expression for Fermi-Dirac distribution function at any at any temperature.

(b) Show that pressure exerted by an assembly of Fermions is proportional to $n^{\frac{5}{3}}$, where n is number density.

(c) Energy distribution for n_i particle in the i^{th} state is given by $n_i = g_i e^{-(\alpha+\beta\varepsilon_i)}$, where α and β are constant, g_i is the single particle states in the i^{th} level. Using equipartition theorem, show that correct thermodynamic interpretation is $\beta = \frac{1}{KT}$. (15+15+20=50 marks)

Q5.(a) Prove that $\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_S} = 1 - \frac{1}{\gamma}$ Where $\gamma = \frac{C_P}{C_V}$ all terms have their usual meaning

(b) The latent heat of vaporisation of ammonia, expressed in jg^{-1} at t^0 C is represented by the equation $L=138.5\,(135-t)^{1/2}-2.48(135-t)$
Calculate the specific heat capacity of ammonia vapour at constant saturation at 35^0 C. The specific of the saturated liquid is $4.82\ jg^{-1}\ K^{-1}$

(c) Six distinguishable particles are distributed over three non-degenerate levels of energies 0, ε and 2ε.
(i) Calculate the total number of microstates of the system.
(ii) Determine the thermodynamic probabilities (TP) for all possible distributions and obtain the total energy of the distribution for which the probability is maximum .
(iii) Using the results of the TP calculations and knowledge of permutation, verify (i).

(15 +15+20 = 50 marks)

T-8-8 16/12/2020

NAME - Mamta Yadav
TEST - Thermal Physics & Statistics
ROLL No - 0829179
TIME - 5:00 pm to 8:00 pm
(on 15th Dec'2020)

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Q1	Q2	Q3	Q4	Q5
25	29	27	30	30

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$\frac{141}{250}$

Q2. (a) The adiabatic demagnetisation cycle of a Paramagnetic specimen is as follows:-

→ The unpaired electrons in the Paramagnetic specimen act as a current loo and constitute a magnetic moment. However, in the absence of external applied field they are randomly oriented and the Net Magnetisation is Zero.

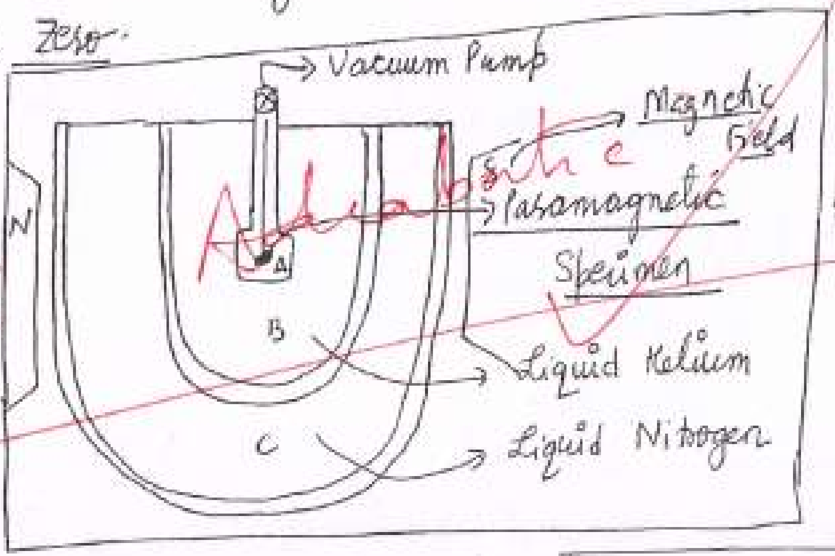


Fig. Setup for Adiabatic Demagnetisation

Adiabatic cycle?

Where is

From the First Law of Thermodynamics, $\boxed{\delta Q = dU + BdM}$

→ ISOTHEMAL MAGNETISATION - Paramagnetic specimen is in Bulb A. Helium gas is introduced in it. This creats a thermal contact with Bulb B (Temp~1.2K). When magnetic field is turned on we get a magnetised specimen which is at $\boxed{T \sim 1.2K}$ as heat generated is removed from A to

→ ADIABATIC DEMMAGNETISATION - Helium gas is evacuated ~~in~~ from bulb A which isolates the body thermally. When field is turned off there is fall in Internal Energy & hence temperature is reduced below 1.2K

$$\delta Q = 0 = dU - BdM \Rightarrow \boxed{dU = \cancel{B(0=M} \; BdM}$$

Mathematical Treatment

The Second T-dS equation for a Paramagnetic substance is as follows:-

$$\boxed{TdS = C_B dT + T\left(\frac{\partial M}{\partial T}\right)_B dB = 0} \rightarrow \text{as the process is Adiabatic}$$

According to the Curie's Law, $M = \frac{kVB}{T}$

$$\boxed{\left(\frac{\partial m}{\partial T}\right)_B = \frac{-kVB}{T^2}} \quad ②$$

$$0 = C_B\,dT + T\left(\frac{-kVB}{T^2}\right)dB \Rightarrow T\,dT = \frac{-kVB\,dB}{C_B}$$

Integrating from T_i to T_f and from B_0 to 0 for demagnetisation

$$T_f^2 - T_i^2 = -\frac{kV}{C_B}\left(0 - B_0^2\right)$$

$$\boxed{\Delta T = T_f - T_i = \frac{kVB}{2C_B T_{av}}}$$ where $T_{av} = \frac{T_i + T_f}{2}$

11/20

~~where~~ This is the required expression

From the expression, the lower the Initial Temperature, T_i, the lower will T_{av} and Hence greater fall in Temperature, ie, $\boxed{\Delta T}$.

Limitations → It can't cool ver large bodies.
→ It can't be used in experiments with no magnetic field
→ They initial temperature must be very low already by using Liquid Helium, Joule-Kelvin effect, etc.

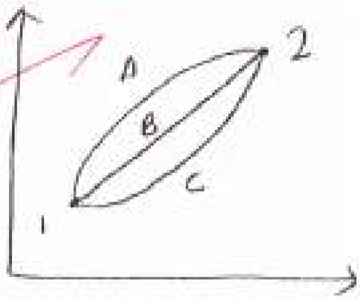
b) Entropy is an extensive variable which gives the extent of intraMolecular Arrangement. It is maximum at equilibrium & therefore, also tells about the probability of occurrence.

According to Clausius Inequality, for a closed loop,

$$\boxed{\oint \frac{\delta Q}{T} \le 0}$$

where inequality is for ir-reversible process and equality is for reversible process.

Consider a process from point 1 to point 2,



$$\boxed{\oint_{1A2B1} \frac{\delta Q}{T} = 0 = \int_{1\ \text{via}\ A}^{2} \frac{\delta Q}{T} + \int_{2\ \text{via}\ B}^{1} \frac{\delta Q}{T}} \text{ —— ①}$$

Also $$\boxed{\oint_{1A2C1} \frac{\delta Q}{T} = 0 \quad \int_{1\ \text{via}\ A}^{2} \frac{\delta Q}{T} + \int_{2\ \text{via}\ C}^{1} \frac{\delta Q}{T}} \text{ —— ②}$$

On comparing, ① & ②, $\displaystyle\int_{2\ \text{via}\ B}^{1} \frac{\delta Q}{T} = \int_{2\ \text{via}\ C}^{1} \frac{\delta Q}{T}$.

Therefore, entropy $\boxed{dS = \frac{\delta Q}{T}}$ is independent of the path taken (B or C) and depends only on the ~~state~~ initial & final state (1

This implies that entropy is a path independent function.

Change in Entropy

From the First Law of Thermodynamics, $\boxed{\delta Q = dU + p\,dV}$

We know, $dS = \frac{\delta Q}{T}$ and $C_v = \left(\frac{\partial Q}{\partial T}\right)_v = \left(\frac{dU}{dT}\right)_v$

using these above, $\boxed{T\,dS = C_v\,dT + p\,dV}$ —— (a)

From Mayer's formula, $C_p - C_v = R$

Further, from Ideal Gas equation of 1 mole, $pV = RT$

∴ $pdV + Vdp = RdT$

Therefore, $\boxed{TdS = C_p\, dT \cancel{+} - Vdp}$ — (b)

Multiplying ⓐ by C_p and ⓑ by C_v & solving,

$$(C_p - C_v)TdS = pC_p dV + VC_v\, dp$$

$$dS = \frac{pC_p}{RT} dV + \frac{VC_v}{RT} dp$$

$$\boxed{dS = C_p \frac{dV}{V} + C_v \frac{dp}{p}}$$ — ©

(i) ΔS in p & V,

from ©, $$\boxed{\Delta S = C_p \log_e \frac{V_f}{V_i} + C_v \log_e \frac{p_f}{p_i}}$$

9/15

(ii) ΔS in p & T,

from ⓑ, $$\boxed{\Delta S = C_p \log_e \frac{T_f}{T_i} - R \log_e \frac{p_f}{p_i}}$$

(iii) ΔS in ~~P~~T & V

from ⓐ, $$\boxed{\Delta S = C_v \log_e \frac{T_f}{T_i} + R \log_e \frac{V_f}{V_i}}$$

entropy's measurement is always in relation to the initial state.

(c) The mean free path can be defined as the average distance travelled by a molecule between two consecutive collisions

Mean Free path: $\boxed{\lambda = \frac{1}{\sqrt{2}\, n \pi d^2}}$

n → Number Density

d → Diameter of molecule

We know from ideal gas equation, $\boxed{pV = n'RT}$ n' = no. of Moles

$$pV = (n'N_A)k_BT \qquad (R = k_B N_A)$$

$$p = \frac{N}{V}k_BT$$

$$\boxed{p = nk_BT}$$

using this above, $\boxed{\lambda = \frac{k_BT}{\sqrt{2}\pi p d^2}}$, ie, $\lambda \propto T$

when the Temperature is doubled, $T' = 2T$

$$\lambda' = 2\lambda$$

$$\boxed{\lambda' = 4\times10^{-7}\,m}$$

9/15

for probability, we know $n = n_0 \exp\left(\frac{-x}{\lambda}\right)$ where n is ~~no~~ no of molecules not colliding.

Probability that a molecule will travel 6×10^{-7} m without collision, $P = \frac{n}{n_0} = \exp\left(-\frac{6\times10^{-7}}{4\times10^{-7}}\right) \Rightarrow \boxed{P = 22.313\%}$

Q3(a) Joule-Kelvin process is the adiabatic expansion of gas from high pressure, p_1 to low pressure, p_2 through a porous plug resulting in fall in temperature.

Joule-Kelvin Coefficient, $\mu = \left(\frac{\partial T}{\partial p}\right)_H$

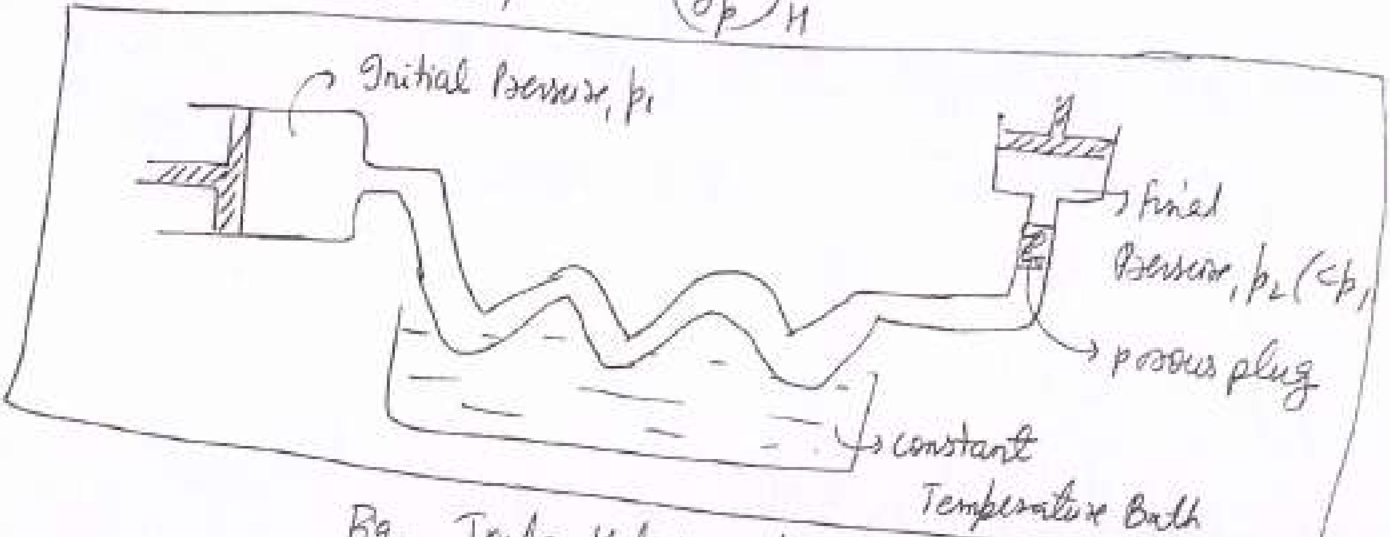


Fig. Joule-Kelvin experiment

Let enthalpy, H be a function of Temperature & Pressure

$$H = H(T, p) \Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

for constant enthalpy, $\left(\frac{\partial H}{\partial p}\right)_H = 0 = \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H + \left(\frac{\partial H}{\partial p}\right)_T$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{-1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T \qquad \text{as } C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\cancel{\partial T}\mu = \frac{-1}{C_p}\left(\frac{\partial (U + pV)}{\partial p}\right)_T$$

$$\boxed{\mu = \frac{-1}{C_p}\left[\left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial p}\right)_T\right]}$$

According to Joules's Law, $\left(\frac{\partial U}{\partial p}\right)_T = 0$ as internal energy of an ideal gas is a function of Temperature only.

According to Boyle's Law, $\partial\ pV = nRT = K$ (as constant T).

∴ $\left[\frac{\partial(pV)}{\partial p}\right]_T = 0$ for an ideal gas.

This implies that the Joule- Kelkin Coefficient is zero. So, there is a no change in temperature in an ideal gas. However, this is not True for Real Gases.

Explanation : — In Real Gases, some work is always in expanding the gas ~~and~~ due to Intermolecular force. Therefore there is a drop in temperature.

If T < Inversion Temperature, Ti ⇒ There is fall in Temperature

If T > Ti ⇒ This is increase in temperature

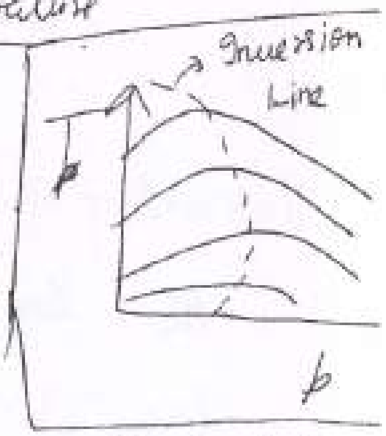


Fig. Constant enthalpy curve for different Initial Pressure

~~Observations~~

9/15

b) from the First Law of Thermodynamics, $\boxed{\delta Q = C_v dT + p dV}$

Adiabatic Process is the process in which heat exchanged is 0, ie,

$\boxed{\delta Q = 0}$.

$$\boxed{0 = C_v dT + p dV} \text{ — ①}$$

from Vander - Waal's equation, $\left(p + \frac{a}{V^2}\right)(V-b) = RT$

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

Ignoring a/V^2 as $a << v$ $\boxed{p = \frac{RT}{V-b}}$ —②

using ② in ①, $0 = C_v dT + RT\frac{dV}{V-b}$

$$0 = \frac{dT}{T} + \frac{C_p - C_v}{C_v}\left(\frac{dV}{V-b}\right)$$

from Mayer's formula, $C_p - C_v = R$

$$0 = \frac{dT}{T} + (\gamma - 1)\frac{dV}{V-b}$$

$[\gamma = C_p/C_v]$

Integrating the above equation,

$$~~K~~ = \log_e T + (\gamma-1)\log_e(V-b)$$

$$\log_e T(V-b)^{\gamma-1} = K$$

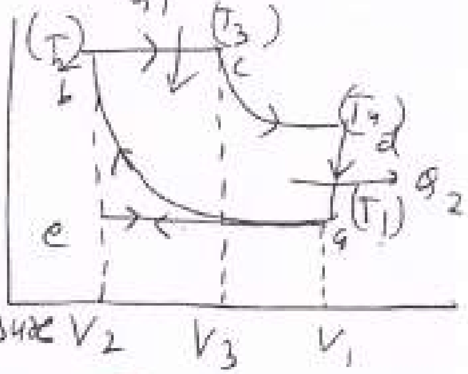
$$\boxed{T(V-b)^{\gamma-1} = K'}$$

✓

6½/10

This is the required relation for the Adiabatic Curve

(c) A Diesel Engine is a four stroke combustion engine which operates in a cyclic process as shown below :-



e → a : Intake Stroke

a → b : Compression stroke in which gas is compressed abiabatically from V_1 to V_2

b → c : Heat Q_1 is absorbed at constant pressure

c → d : Power Stroke in which gas is expanded abiabatically from V_3 to V_1

d → a : Heat Q_2 is released at constant volume.

a → e : exhaust Stroke

From abiabatic equation, $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$

for a → b : $\cancel{T_2} T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$ —— ①

for c → d : $T_3 V_3^{\gamma-1} = T_4 V_1^{\gamma-1}$ —— ②

For efficiency $\eta = 1 - \frac{Q_2}{Q_1}$ (ratio of Work Done per cycle to Heat Absorbed per Cycle)

$$\eta = 1 - \frac{nC_v(T_4 - T_1)}{nC_p(T_3 - T_2)}$$

$$\eta = 1 - \frac{1}{\gamma}\frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)} \quad \text{—— ③}$$

Taking Compression Ratio, $\rho_c = \frac{V_1}{V_2}$ and Expansion Ratio, $r_c = \frac{V_3}{V_2}$

using ① & ② $\eta = 1 - \frac{1}{\gamma}\frac{1}{\rho_c^{\gamma-1}}\left[\frac{(T_3/T_2) r_c^{\gamma-1} - 1}{T_3/T_2 - 1}\right]$

Since b → c is at constant pressure, from ideal gas equation

$\frac{V}{T}$ is constant, $\frac{V_3}{V_2} = \frac{T_3}{T_2} = r_c$

Therefore, $$\boxed{\eta = 1 - \frac{1}{\gamma \rho_c^{\gamma-1}}\left(\frac{r_c^{\gamma}-1}{r_c-1}\right)}$$ - efficiency of Diesel Engine

Consider a carnot cycle working between Highest & Lowest Temperature, T_3 and T_1,

efficiency, $$\boxed{\eta' = 1 - \frac{T_1}{T_3}}$$

from ③, efficiency of Diesel Cycle is $\eta = 1 - \frac{T_1}{T_2}(A)$ where

$A = \frac{T_4/T_1 - 1}{\gamma(T_3/T_2 - 1)}$

9½ / 15

as $T_3 > T_2$

$\frac{T_1}{T_3} < \frac{T_1}{T_2}$

$1 - \frac{T_1}{T_3} > 1 - \frac{T_1 A}{T_2}$ (A is ~~greater~~ less than 1, as $\gamma > 1$)

$$\boxed{\eta_{car} > \eta_{die}}$$

Therefore, efficiency of carnot engine is more. This is in accordance with Carnot Theorem.

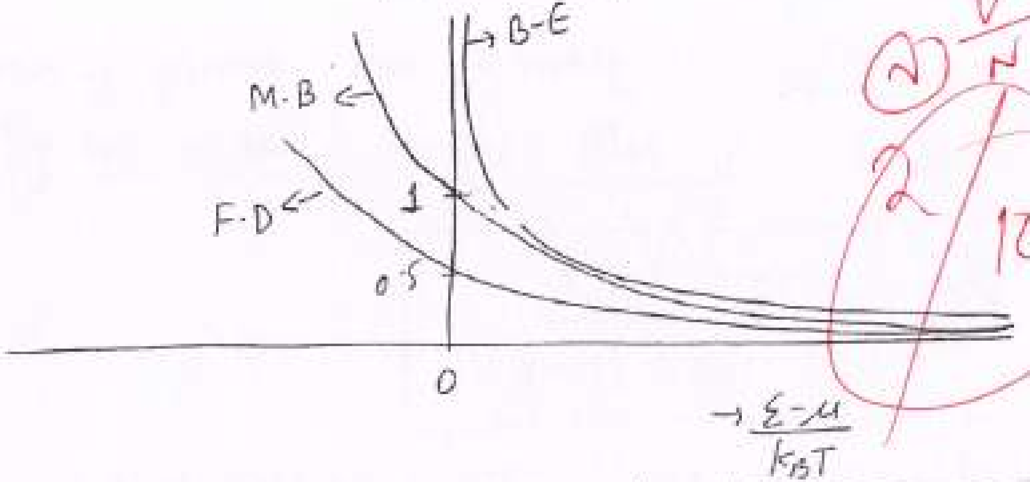
(d) There are two Quantum Statistical Distributions, Fermi-Dirac (for Half-integral Particles) and Bose-Einstein (for Integral Spin Particles).

Distribution function,
$$\boxed{n = \frac{1}{\exp\left(\frac{\varepsilon-\mu}{k_BT}\right)+K}}$$

where K = +1 for Fermi-Dirac
K = -1 for Bose-Einstein
K = 0 for Maxwell Boltzmann

① $\frac{g_i}{N}$ is large for Quantum to classical

② $\frac{V}{N}\frac{(3mkT)^{3/2}}{h^3} >> 1$



2/10

Therefore, there is convergence when $\boxed{\left(\frac{\varepsilon-\mu}{k_BT}\right) \rightarrow 0}$

$\boxed{\mu}$ → μ is the Chemical Potential. It is the change in energy due to gain or loss in Particles

For, Fermions, μ = Fermi Energy = E_F (ie, energy of highest le at 0K)

For, Bosons, μ = 0 for Photons (as they are not conserved & can be neglected for Low Temperature due to Bose-einstein condensation.

Q4: Fermi-Dirac is for fermions

- They have Half-Integral Spin Particles
- They are Indistinguisable
- They follow Pauli's exclusion Principle
- They have Anti-symmetric Wave function

Let there be $n_1, n_2, n_3 . n_i \ldots$ fermions in ~~energ~~ levels of energy $\varepsilon_1, \varepsilon_2, \varepsilon_3 \ldots \varepsilon_i \ldots$ having degeneracy $g_1, g_2 \ldots$

Due to Pauli's exclusion principle, no two fermions can ~~have~~ occupy same energy level, ie, $\boxed{n_i \leq g_i}$

So, no. of ways in which n_i fermions can occupy g_i levels is no. of ways in which n_i cells can be choosen out of g_i.

$$\boxed{\Omega_{FE} = \prod {}^{g_i}C_{n_i} = \prod \frac{(g_i)!}{(n_i)!\,(n_i - g_i)!}}$$

For distribution function, Ω_{FE} is maximum subject to the constraints,

$$\sum n_i = N \ (\text{constant}) \rightarrow \sum \delta n_i = 0$$

$$\sum n_i \varepsilon_i = E \ (\text{constant}) \rightarrow \sum \varepsilon_i \delta n_i = 0$$

$$\log_e \Omega = \sum \left[\log_e g_i! - \log_e (n_i)! - \log_e (g_i - n_i)! \right]$$

$$= \sum \left[g_i \log_e g_i - g_i - n_i \log_e n_i + n_i - (g_i - n_i) \log_e (g_i - n_i) + (g_i - n_i) \right]$$

$$\delta \log_e \Omega = \sum \underset{\substack{=0 \\ [\text{as } g_i \text{ is constant}]}}{\delta (g_i \log_e g_i - g_i)} - \delta n_i \log_e n_i + \cancel{\frac{n_i \delta n_i}{n_i}} \cancel{+ \delta n_i} - \delta (g_i - n_i) \log_e$$

$$- \cancel{\frac{g_i - n_i}{g_i - n_i}} (-\delta n_i) + \cancel{\delta (g_i - n_i)}$$

$$\delta \log_e \Omega = \sum \delta n_i \log_e\left(\frac{n_i}{g_i - n_i}\right)$$

for Distribution function, $\delta(\log_e \Omega) = 0$. Further using Lagrang's Method of undetermined multiplier to relax the constants,

$$\sum \delta n_i \left(\log_e\left(\frac{n_i}{g_i-n_i}\right) + \alpha + \beta\varepsilon_i\right) = 0$$

$$\log_e\left(\frac{n_i}{g_i-n_i}\right) + \alpha + \beta\varepsilon_i = 0$$

9/15

$$\frac{n_i}{g_i - n_i} = \exp[(\alpha + \beta\varepsilon_i)]$$

$$\boxed{n_i = \frac{g_i}{1 + \exp - (\alpha + \beta\varepsilon_i)}}$$

This is the required Distribution Function.

b) For fermions, Occupancy number, $n_{FE} = \dfrac{1}{\exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right) + 1}$

Density of States, $D(\varepsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \varepsilon^{1/2}$

Number of Fermions, $\boxed{N = \int_0^{\infty} D(\varepsilon)\, n(\varepsilon)\, d\varepsilon}$

at $T=0$, $n(\varepsilon) = 1$ for $\varepsilon < \varepsilon_F$
$= 0$ for $\varepsilon > \varepsilon_F$

$$N = \int_0^{\varepsilon_F} 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \varepsilon^{1/2}\, d\varepsilon$$

$$\boxed{N = \frac{8\pi V}{3}\left(\frac{2mE_F}{h^2}\right)^{3/2}} \quad \text{—①}$$

~~Similarly,~~ $~~E = \int \varepsilon\, dn = \int_0^\infty \varepsilon D(\varepsilon) n(\varepsilon)\, d\varepsilon~~$

from ①,

$$\boxed{E_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}}$$

$~~E = \int 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \varepsilon^{3/2}\, d\varepsilon~~$

$~~\boxed{E = \frac{8\pi V}{5}\left(\frac{2mE_F}{h^2}\right)^{3/2} E_F}~~$ —②

~~from ① & ②,~~ $~~E = \frac{3}{5} N E_F~~$

we know, Pressure, $p = \frac{2}{3}\left(\frac{N}{V}\right) E_F$

$$p = \frac{2}{3}\left(\frac{N}{V}\right)\frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$$

$$\boxed{p \propto \left(\frac{N}{V}\right)^{5/3}}$$

9/15

where $n = \frac{N}{V}$ is the Number Density

(c) Energy Distribution for n_i particles in the ith State is,

$$\boxed{n_i = g_i e^{-\alpha} e^{-\beta\varepsilon_0}}$$

Total Number of Particles, $N = \sum n_i = \sum g_i e^{-\alpha} e^{-\beta\varepsilon_i}$

In terms of integration, $N = \int D(\varepsilon) e^{-\alpha} e^{-\beta\varepsilon} d\varepsilon$

$$\boxed{N = \int_0^\infty 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} e^{-\alpha} \varepsilon^{1/2} e^{-\beta\varepsilon} dE} \text{ — ①}$$

Similarly, Total Energy of Particles, $E = \int \varepsilon D(\varepsilon) e^{-\alpha} e^{-\beta\varepsilon} d\varepsilon$

$$\boxed{E = \int 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} e^{-\alpha} \varepsilon^{3/2} e^{-\beta\varepsilon} dE} \text{ — ②}$$

The average energy is,

$$\bar{E} = \frac{E}{N} = \frac{\int_0^\infty \cancel{4\pi V \left(\frac{2m}{h^2}\right)^{3/2} e^{-\alpha}} \varepsilon^{3/2} e^{-\beta\varepsilon} dE}{\int_0^\infty \cancel{4\pi V \left(\frac{2m}{h^2}\right)^{3/2} e^{-\alpha}} \varepsilon^{1/2} e^{-\beta\varepsilon} dE} = \frac{\int_0^\infty \varepsilon^{3/2} e^{-\beta\varepsilon} d\varepsilon}{\int_0^\infty \varepsilon^{1/2} e^{-\beta\varepsilon} d\varepsilon}$$

Using gamma function integral $\int_0^\infty x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}}$

$$\bar{E} = \frac{\frac{\Gamma(5/2)}{\beta^{5/2}}}{\frac{\Gamma(3/2)}{\beta^{3/2}}} = \frac{\frac{3\,\cancel{\Gamma(3/2)}}{2\,\beta}}{\cancel{\Gamma(3/2)}} \Rightarrow \boxed{\bar{E} = \frac{3}{2\beta}} \text{ — ⑦}$$

According to the Law of Equipartition of Energy, average energy with each d.o.f. (degree of freedom) is $\frac{k_B T}{2}$. Since a particle has 3 d.o.f.

$$\boxed{\overline{E} = \frac{3K_BT}{2}} \text{ — } ②$$

from ① & ②,

$$\frac{3}{2\beta} = \frac{3K_BT}{2}$$

$$\Rightarrow \boxed{\beta = \frac{1}{K_BT}}$$

This is the required thermodynamic interpretation.

12/20

Q5 (a) To prove, $\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial T}\right)_S} = 1 - \frac{1}{\gamma}$

R.H.S. $= 1 - \frac{1}{\gamma} = 1 - \frac{1}{C_p/C_V} = \frac{C_p - C_V}{C_p}$ — ①

Now, Let us consider entropy to be a function of Volume V and temperature T.

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

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

[Using Ist Maxwell Relat $\rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

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

$$\left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\delta Q}{\partial T}\right)_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p} \quad \text{—②}$$

9/15

using ② in ①,

$$R.H.S = \frac{T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p}{T\left(\frac{\partial S}{\partial T}\right)_p} = \frac{\cancel{T}\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_p}$$

from IVth Maxwell relation: $\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$

& R.H.S = $\left(\frac{\partial p}{\partial T}\right)_V$ = L.H.S.

Hence proved.

b). Latent Heat of Vapourisation can be defined as the amount of Heat Released when vapour is converted into liquid at constant temperature.

We know, change ~~p~~ in entropy per unit mass for conversion of vapour into liquid.

$$S_2 - S_1 = \frac{L}{T}$$

Differentiating w.r.t. t, $\frac{\partial S_2}{\partial T} - \frac{\partial S_1}{\partial T} = \frac{1}{T}\frac{\partial L}{\partial T} - \frac{L}{T^2}$

$$T\frac{\partial S_2}{\partial T} - T\frac{\partial S_1}{\partial T} = \frac{\partial L}{\partial T} - \frac{L}{T}$$

$$(C_2)_{Liq} - (C_1)_{vap} = \frac{dL}{dT} - \frac{L}{T}$$

given, $L = 138.5\,(135-t)^{1/2} - 2.48\,(135-t)\ Jg^{-1}$

$$\frac{\partial L}{\partial T} = \frac{138.5 \times 1/2\,[-1]}{(135-t)^{1/2}} - 2.48(-1)$$

$$\frac{\partial L}{\partial T} = \frac{-69.25}{\sqrt{135-t}} + 2.48$$

9/15

using, $T = 35^\circ C = 308\,K$, $(C_1)_{vap} = 4.82\ Jg^{-1}K^{-1}$

$$(C_2) \text{ at } 35^\circ C = 4.82 - \frac{69.25}{\sqrt{135-35}} + 2.48 + \frac{138.5\,(135-35)^{1/2}}{308} + \frac{248 \times (135-35)}{308}$$

$$\boxed{C_2 = -3.3167\ Jg^{-1}K^{-}}$$

-ve sign indicates heat is released-

(i) as the particles are Distinguishable, the Maxwell-Boltzmann distribution will be followed.

(i) $n_i = 6$

$g_i = 3 \; (0, \varepsilon, 2\varepsilon)$

No. of Microstates $= g_i^{n_i} = 3^6 = \underline{\underline{729}}$.

(ii) No. of Macrostates are → 6, 0, 0 → ~~${}^6C_6 \times {}^3C_1 = 3$~~ (${}^6C_6$ → choosing 6 particles out of 6; ${}^3C_1$ → choosing 1 out of 3)

→ 5, 1, 0 : ~~36~~

→ 4, 2, 0 : ~~90~~

→ 3, 3, 0 :

→ 4, 1, 1

→ 3, 2, 1

→ 2, 2, 2

12/20

for Maxwell-Boltzmann, the no of macrostates is $\Omega = \dfrac{N!}{\prod n_i!}$

Distribution	Macrostate	Microstate
6, 0, 0	$= \dfrac{6!}{6!0!0!} = 1$	$1 \times {}^3C_1 = 3$
5, 1, 0	$= \dfrac{6!}{5!1!0!} = 6$	$6 \times {}^3C_1 \times {}^2C_1 = 6 \times 3! = 36$
4, 2, 0	$= \dfrac{6!}{4!2!0!} = 15$	$15 \times {}^3C_1 \times {}^2C_1 = 15 \times 6 = 90$
3, 3, 0	$= \dfrac{6!}{3!3!0!} = 20$	$20 \times {}^3C_2 \times \cancel{{}^2C_1} = 20 \times 3 = \cancel{120}\ 60$
4, 1, 1	$= \dfrac{6!}{4!1!1!} = 30$	$30 \times {}^3C_2 = 90$
3, 2, 1	$= \dfrac{6!}{3!2!1!} = \dfrac{6 \times 5 \times 4}{2} = 60$	$30 \times {}^3C_2 \times {}^2C_1 = 90$
2, 2, 2	$= \dfrac{6!}{} = 90$	$90 \times {}^3C$ = 90

${}^nC_m = \dfrac{n!}{m!(n-}$

When all are added →

The maximum number of macrostates corresponds to the configuration $(2, 2, 2)$.

Therefore, its total energy is

$$E = \sum \varepsilon_i n_i = 2\times 0 + 2\times \varepsilon + 2\times 2\varepsilon$$

$$\boxed{E = 6\varepsilon}$$

Q: (a) from the Clausius- Clapesoyon Equation,

$$\frac{dp}{dT} = \frac{T}{L(V_{liq} - V_{sol})}$$

where $L \rightarrow$ Latent Heat of fusion $= 24.5 \times 10^{7}\ \mathrm{erg\,g^{-1}} = 24.5\ \mathrm{J\,g^{-1}}$

$V_{liq}, V_{sol} \rightarrow$ Specific Volume in Liquid & Solid Phase

at $p_1 = 1$ atm , $T_1 = 600$ k

$p_2 = 100$ atm , $T_2 = ?$

2

$$dT = \frac{L\,dp\,(V_{liq} - V_{sol})}{T} = \frac{L\,dp}{T}\left(\frac{1}{\rho_{liq}} - \frac{1}{\rho_{sol}}\right)$$

$$dT = \frac{24.5\ \mathrm{J\,g^{-1}} \times 99 \times 1.01325 \times 10^{5}\ \mathrm{Pa}}{600\,\mathrm{K}}\left(\frac{1}{10.65\,\mathrm{g\,cm^{-3}}} - \frac{1}{11.01\,\mathrm{g\,cm^{-3}}}\right)$$

$$\boxed{dT = 1.2575 \times 10^{-3}\ \mathrm{K}}$$

This is the change in the Melting Point.

→ Clausius Clapeyron Equation is obeyed to a very good ~~ext~~ accuracy by all first-order phase transitions b). C_p can be defined as the heat required to change the Temperature of a body by unit °C/K as constant pres

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p$$

from second Maxwell's Relations,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Differentiating w.r.t. t. at constant p.

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T\right]_p = -\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

S is an exact differential, ∴, $\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T\right]_p = \left[\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p\right]_T$

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p\right]_T = -\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

$$\left[\frac{\partial}{\partial p}\left(\frac{T\partial S}{\partial T}\right)_p\right]_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

We know $T\partial S = \delta Q$

$$\boxed{\left[\frac{\partial C_p}{\partial p}\right]_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p}$$

6½ / 10

given $V = \frac{RT}{p} - \frac{C}{T^3}$ $\Rightarrow$ $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{3C}{T^4}$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0 - \frac{12C}{T^5}$$

$\boxed{\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{12C}{T^4}}$ → Required Answer.

(i) Entropy is a state variable which gives the ~~order~~ extent of disorder in molecular arrangement of the system

$$\Delta S = \int dS = \int \frac{\delta Q}{T}$$

as the Temperature, T is constant at 27°C

$$\boxed{\Delta S = \frac{1}{T}\int \delta Q}$$

δQ = Power generated = $VI = I^2R$

$\delta Q = (10A)^2 \times 250\Omega$

$\delta Q = 2.5 \times 10^4$ Joules

$$\Delta S = \frac{2.5\times10^4}{(273+27)} \Rightarrow \boxed{\Delta S = 83.33 JK^{-1}}$$

6½/10

According to the ~~Third &~~ Second Law of thermodynamic, the total change in the entropy of the universe in a reversible reaction is zero

$$\Delta S_{sys} + \Delta S_{surrounding} = 0$$

Therefore, $\boxed{\Delta S_{surr} = -83.33 JK^{-1}}$

d) Vander-Waal Equation – $\left(p+\frac{a}{V^2}\right)(V-b) = RT$

T_c is the Critical Temperature above which liquefication of a gas is not possible, not matter how high the pressure is.

Relation between Critical Constants & a, b is

$V_c = 3b$, $T_c = \frac{8a}{27Rb}$, $p_c = \frac{a}{27b^2}$ given $T_C = 5.3\,K$

$P_c = 2.25\,atm$

$= 2.25 \times 1.01325 \times 10^5$

$b = \frac{RT_c}{8p_c}$ $\boxed{b = 2.4148 \times 10^{-5}\ m^3 mol}$ ✓

$a = 27b^2 p_c$ $\boxed{a = 3.5895 \times 10^{-3}\ J m^3 mol^{-2}}$ ✓

3/5

From the Correction Term due to finite size of Gas Molecules, we know, $b = 4V_m$ where V_m = volume of Molecule

$V_m = \frac{b}{4}$

$V_m = \frac{4}{3}\pi r^3 = \frac{b}{4}$

$r^3 = \frac{3b}{16\pi}$

2/5

5/10

Therefore, Diameter of Helium Molecule $= 2.2591 \times 10^{-2}\ m.$

e) Viscosity can be defined as the property by the virtue of which relative motion between layers of fluids is resisted. In gases, it is due to collision between molecules caused by random motion.

$$\eta = \frac{mn\bar{v}\lambda}{3}$$

where λ (mean free path) $= \dfrac{1}{\sqrt{2}n\pi d^2}$

Average Velocity, $\bar{v} = \sqrt{\dfrac{8k_BT}{m\pi}} = \sqrt{\dfrac{8\times1.38\times10^{-23}\times288}{32\times1.67\times10^{-27}\times\pi}}$

$T = 15^\circ C = 288\,K$

$$\boxed{\bar{v} = 435.1837\ ms^{-1}}$$

$\eta = 196\times10^{-6}$ Poise (cgs units) $= 196\times10^{-5}$ ~~mks~~ $kg\,m^{-1}s^{-1}$

$$\eta = \frac{m\bar{v}}{3\sqrt{2}\pi d^2}$$

$$d = \sqrt{\frac{m\bar{v}}{3\sqrt{2}\eta\pi}}$$

$$\boxed{d = 0.2984\ \mathring{A}}$$

5/10

2.984 Å