#### Molecules and Crystals (Part - 1)

### Q.167. Determine the angular rotation velocity of an $S_2$ molecule promoted to the first excited rotational level if the distance between its nuclei is d = 189 pm.

**Ans**. In the first excited rotational level J = 1

$$E_{I} = 1 \times 2 \frac{\hbar^{2}}{2I} = \frac{1}{2} I \omega^{2} \text{ classically}$$

Thus  $\omega = \sqrt{2} \frac{\hbar}{I}$ 

Now 
$$I = \sum m_i r_i^2 = \frac{m}{2} \frac{d^2}{4} + \frac{m}{2} \frac{d^2}{4} = m \frac{d^2}{4}$$

where m is the mass of the mole cub and  $r_i$  is the distance of the atom from the axis.

$$\omega = \frac{4\sqrt{2}\hbar}{m\,d^2} = 1.56 \times 10^{11}\,\mathrm{rad/s}$$

Thus

#### Q.168. For an HCl molecule find the rotational quantum numbers of two neighbouring levels whose energies differ by 7.86 meV. The nuclei of the molecule are separated by the distance of 127.5 pm.

**Ans.** The axis of rotation passes through die centre of mass of the HCl molecule. The distances of the two atoms from the centre of mass are

$$d_H = \frac{m_{Cl}}{m_{HCl}}d, \ d_{Cl} = \frac{m_H}{m_{HCl}}d$$

Thus I - moment of inertia about the axis

$$= \frac{4}{2} m_H d_H^2 + m_{Cl} d_{Cl}^2 = \frac{m_H m_{Cl}}{m_H + m_{Cl}} d^2$$

The energy difference ^between two neighbouring levels whose quantum numbers are J & J - 1 is

$$\frac{\hbar^2}{2I} \cdot 2J = \frac{J\hbar^2}{I} = 7.86 \text{ meV}$$

Hence J = 3 and the levels have quantum numbers 2 & 3,

### Q.169. Find the angular momentum of an oxygen molecule whose rotational energy is E = 2.16 meV and the distance between the nuclei is d = 121 pm.

Ans. The angular momentum is

 $\sqrt{2IE} = M$ 

Now  $I = \frac{m d^2}{4}$  (m = mass of O<sub>2</sub> molecule) = 1.9584 x 10<sup>-39</sup> gm c<sup>2</sup>

So  $M = 3.68 \times 10^{-27}$  erg sec. = 3.49 h

(This corresponds to J = 3)

Q.170. Show that the frequency intervals between the neighbouring spectral lines of a true rotational spectrum of a diatomic molecule are equal. Find the moment of inertia and the distance between the nuclei of a CH molecule if the intervals between the neighbouring lines of the true rotational spectrum of these molecules are equal to  $\Delta \omega = 5.47.10^{12} \text{ s}^{-1}$ .

**Ans.** From 
$$E_J = \frac{\hbar^2}{2I}J(J+1)$$

and the selection rule  $\Delta J = 1$  or  $J \rightarrow J - 1$  for a pure rotational spectrum we get

$$\omega\left(J,J-1\right)\,=\,\frac{\hbar J}{I}$$

Thus transition lines are equispaced in frequency

 $\Delta \omega = \frac{\hbar}{I}.$ 

In the case of CH molecule

$$I = \frac{\hbar}{\Delta \omega} = 1.93 \times 10^{-40} \,\mathrm{gm} \,\mathrm{cm}^2$$

 $I = \frac{m_c m_H}{m_c + m_H} d^2$ Also

so 
$$d = 1.117 \text{ x } 10^{-8} \text{ cm} = 111.7 \text{ pm}$$

#### Q.171. For an HF molecule find the number of rotational levels located between the zeroth and first excited vibrational levels assuming rotational states to be independent of vibrational ones. The natural vibration frequency of this molecule is equal to 7.79.10<sup>14</sup> rad/s, and the distance between the nuclei is 91.7 pm.

Ans. if the vibrational frequency is to 0 the excitation energy of the first vibrational level will be  $\frac{1}{2}$  o. Thus if there are J rotational levels contained in the band between the ground state and the first vibrational excitation, then

$$\hbar \omega_0 = \frac{J(J+1)\hbar^2}{2I}$$

where as stated in the problem we have ignored any coupling between the two. For HF molecule

$$I = \frac{m_H m_F}{m_H + m_F} d^2 = 1.336 \times 10^{-4} \,\mathrm{gm \, cm}^2$$

Then 
$$J(J+1) = \frac{2I\omega_0}{\hbar} = 197.4$$

For J = 14, J (J + 1) = 210. For J - 13, J (J + 1) = 182. Thus there lie 13 levels between the ground state and the first vibrational excitation.

Q.172. Evaluate how many lines there are in a true rotational spectrum of CO molecules whose natural vibration frequency is  $\omega = 4.09.10^{14} \text{ s}^{-1}$  and moment of inertia I = 1.44.10<sup>-39</sup>g•cm<sup>2</sup>.

Ans. We proceed as above. Calculating  $\frac{2I\omega_0}{\hbar}$  we get  $\frac{2I\omega_0}{\hbar} = 1118$ 

Now this must equal  $J(J+1) = \left(J + \frac{1}{2}\right)^2$ 

Taking the square root we get J = 33.

Q.173. Find the number of rotational levels per unit energy interval, dN/dE, for a diatomic molecule as a function of rotational energy E. Calculate that magnitude for an iodine molecule in the state with rotational quantum number J = 10. The distance between the nuclei of that molecule is equal to 267 pm.

Ans. From the formula

$$J(J+1)\frac{\hbar^{2}}{2I} = E$$
  
we get  $J(J+1) = 2IE/\hbar^{2}$   
or  $\left(J+\frac{1}{2}\right)^{2} - \frac{1}{4} = \frac{2IE}{\hbar^{2}}$ 

Hence 
$$J = -\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2IE}{\hbar^2}}$$

writing 
$$J = -\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2IE}{\hbar^2}}$$

$$J + 1 = -\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2I}{\hbar^2}(E + \Delta E)}$$

$$1 = \sqrt{\frac{1}{4} + \frac{2I}{\hbar^2}E + \frac{2I}{\hbar^2}\Delta E} - \sqrt{\frac{1}{4} + \frac{2IE}{\hbar^2}}$$

we find

$$= \sqrt{\frac{1}{4} + \frac{2I}{\hbar^2}E} \left[ \left( 1 + \frac{\Delta E}{E + \frac{\hbar^2}{8I}} \right)^{1/2} - 1 \right]$$
$$= \sqrt{\frac{1}{4} + \frac{2I}{\hbar^2}E} \cdot \frac{\Delta E}{2\left(E + \frac{\hbar^2}{8I}\right)}$$
$$= \sqrt{\frac{2I}{\hbar^2}} \frac{\Delta E}{2\sqrt{E + \frac{\hbar^2}{8I}}}$$

The quantity  $\frac{dN}{dE}$  is  $\frac{1}{\Delta E}$ . For laige E it is

$$\frac{dN}{dE} - \sqrt{\frac{I}{2\hbar^2 E}}$$

For an iodine molecule  $I=m_{\rm i}d^2\!/\ 2=7^*57\ x\ 10^{\cdot 38}\ gm\ cm^2$  Thus for J=10

$$\frac{dN}{dE} = \sqrt{\frac{I}{2\hbar^2 \cdot \frac{\hbar^2}{2I}J(J+1)}} = \frac{I}{\sqrt{J(J+1)}\hbar^2}$$

Substitution gives

 $\frac{dN}{dE} = 1.04 \times 10^4 \text{ levels per eV}$ 

Q.174. Find the ratio of energies required to excite a diatomic molecule to the first vibrational and to the first rotational level. Calculate that ratio for the following molecules:

Molecule	$\omega$ , 10 <sup>14</sup> s <sup>-1</sup>	d, pm
(a) H <sub>2</sub>	8.3	74
(b) HI	4.35	160
(c) I <sub>2</sub>	0 40	267

Here  $\boldsymbol{\omega}$  is the natural vibration frequency of a molecule, d is the distance between nuclei.

Ans. For the first rotational level

$$E_{rot} = 2\frac{\hbar^2}{2I} = \frac{\hbar^2}{I}$$
 and

for the first vibrational level  $E_{vib} = \hbar \omega$ 

$$\xi = \frac{E_{vib}}{E_{rof}} = \frac{I\omega}{\hbar}$$

Here  $\omega$  = frequency of vibration. Now

$$I = \mu d^2 = \frac{m_1 m_2}{m_1 + m_2} d^2.$$

(a) For  $H_2$  molecule I = 4-58 x 10<sup>-41</sup> gm cm<sup>2</sup> and  $\xi$  - 36 (b) For HI molecule, I = 4.2 47 x 10<sup>-40</sup> gmcm<sup>2</sup> and  $\xi$  - 175 (c) For  $I_2$  molecule I = 7.57 x 10<sup>-38</sup>gmcm<sup>2</sup> and  $\xi$  = 2872

Q.175. The natural vibration frequency of a hydrogen molecule is equal to  $8.25.10^{14}$  s<sup>-1</sup>, the distance between the nuclei is 74 pm, Find the ratio of the number of these molecules at the first excited vibrational level (v = 1) to the number of molecules at the first excited rotational level (J = 1) at a temperature T = 875 K. It should be remembered that the degeneracy of rotational levels is equal to 2J + 1.

Ans. The energy of the molecule in the first rotational level will be  $\frac{\hbar^2}{I}$ . The ratio of tire number of molecules at tire first excited vibrational level to the number of molecules at the first excited rotational level is

$$\frac{e^{-\hbar\omega/kT}}{(2J+1)e^{-\hbar^2 J(J+1)/2/kT}}$$
  
=  $\frac{1}{3}e^{-\hbar\omega/kT} \times e^{-\hbar^2/kT} = \frac{1}{3}e^{-\hbar(\omega-2B)/kT}$ 

where

B = h / 2I

For the hydrogen molecule  $I = \frac{1}{2}m_H d^2$ 

$$= 4.58 \times 10^{-41} \text{ gm cm}^2$$

Substitution gives 3.04 x 10<sup>-4</sup>

Q.176. Derive Eq. (6.4c), making use of the Boltzmann , distribution. From Eq. (6.4c) obtain the expression for molar vibration heat capacity  $C_v$  vib of diatomic gas. Calculate  $C_v$ vib for  $Cl_2$  gas at the temperature 300 K. The natural vibration frequency of these molecules is equal to  $1.064 \cdot 10^{14} \text{ s}^{-1}$ 

80

Ans. By definition

$$< E > - \frac{\sum E_{\nu} e^{-E_{\nu}/kT}}{\sum \exp\left(-E_{\nu}/kT\right)} = \frac{\frac{\partial}{\partial \beta} \sum_{\nu=0} e^{-\beta E_{\nu}}}{\sum_{\nu=0}^{\infty} e^{-\beta E_{\nu}}}$$

$$= -\frac{\partial}{\partial\beta} \ln \sum_{\nu=0}^{\infty} e^{-\beta(\nu+L/2)\hbar\omega}, \beta = \frac{1}{kT}$$
$$= -\frac{\partial}{\partial\beta} \ln e^{-1/2\beta\hbar\omega} \frac{1}{1-e^{-\beta\hbar\omega}}$$
$$= -\frac{\partial}{\partial\beta} \left[ -\frac{1}{2}\hbar\omega\beta - \ln\left(1-e^{-\beta\hbar\omega}\right) \right]$$
$$= \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}.$$

Thus for one gm mole of diatomic gas

$$C_{V_{1,\infty}} = N \frac{\partial \langle E \rangle}{\partial T} = \frac{R \left(\frac{\hbar \omega}{kT}\right)^2 e^{\pi \omega/kT}}{\left(e^{\pi \omega/kT} - 1\right)^2}$$

where R = Nk is the gas constant

In the present case 
$$\frac{\hbar \omega}{KT} = 2.7088$$

and 
$$C_{V_{1,\infty}} = 0.56 R$$

Q.177. In the middle of the rotation--vibration band of emission spectrum of HCl molecule, where the "zeroth" line is forbidden by the selection rules, the interval between neighbouring lines is  $\Delta \omega = = 0.79.10^{13}$ s<sup>-1</sup>. Calculate the distance between the nuclei of an HCl molecule.

Ans. In the rotation vibration band the main transition is due to change in vibrational quantum number  $v \rightarrow v - 1$ . Together with this rotational quantum number may change. The "Zcroeth line"  $0 \rightarrow 0$  is forbidden in this case so the neighbouring lines arise due to  $1 \rightarrow 0$  or  $0 \rightarrow 1$  in the rotational quantum number. Now

$$E = E_v + \frac{\hbar^2}{2I} J(J+1)$$

$$\hbar \omega = \hbar \omega_0 + \frac{\hbar^2}{2I} (\pm 2)$$
Thus

-

$$\Delta \omega = \frac{2\hbar}{I} = \frac{2\hbar}{\mu d^2}$$

Hence

so

$$d - \sqrt{\frac{2\hbar}{\mu \Delta \omega}}$$

Substitution gives d = 0.128 nm.

Q.178. Calculate the wavelengths of the red and violet satellites, closest to the fixed line, in the vibration spectrum of Raman scattering by  $F_2$  molecules if the incident light wavelength is equal to  $\lambda_0 = 404.7$  nm and the natural vibration frequency of the molecule is  $\omega = 2.15.10^{14}$  s<sup>-1</sup>.

**Ans.** If  $\lambda_R$  = wavelength of the red satellite

and  $\lambda_v$  = wavelength of the violet satellite

$$\frac{2\pi\hbar c}{\lambda_R} = \frac{2\pi\hbar c}{\lambda_0} - \hbar\omega$$

then

$$\frac{2\pi\hbar c}{\lambda_V} = \frac{2\pi\hbar c}{\lambda_0} + \hbar\omega$$

and

Substitution gives

$$\lambda_R = 424.3 \text{ nm}$$
$$\lambda_V = 386.8 \text{ nm}$$

The two formulas can be combined to give

$$\lambda = \frac{2\pi c}{\frac{2\pi c}{\lambda_0} \mp \omega} = \frac{\lambda_0}{1 \mp \frac{\lambda_0 \omega}{2\pi c}}$$

Q.179. Find the natural vibration frequency and the quasielastic force coefficient of an  $S_2$  molecule if the wavelengths of the red and violet satellites, closest to the fixed line, in the vibration spectrum of Raman scattering are equal to 346.6 and 330.0 nm.

Ans. As in the previous problem

$$\omega = \pi c \left( \frac{1}{\lambda_{\nu}} - \frac{1}{\lambda_{R}} \right) = \frac{\pi c \left( \lambda_{R} - \lambda_{\nu} \right)}{\lambda_{R} \lambda_{\nu}} = 1.368 \text{ x } 10^{14} \text{ rad/s}$$

The force constant x is defined by

$$x = \mu \omega^2$$

where  $\mu$ = reduced mass of the S<sub>2</sub> molecule.

Substitution gives x = 5.01N/cm

Q.180. Find the ratio of intensities of the violet and red satellites, closest to the fixed line, in the vibration spectrum of Raman scattering by  $Cl_2$  molecules at a temperature T = 300 K if the natural vibration frequency of these molecules is  $\omega = 1.06.10^{14} \text{ s}^{-1}$ . By what factor will this ratio change if the temperature is doubled?

Ans. The violet satellite arises from the transition  $1\rightarrow 0$  in the vibrational state of the scattering molecule while the red satellite arises from the transition  $0 \rightarrow 1$ . The intensities of these two transitions are in the ratio of initial populations of the two states i.e. in the ratio

$$\frac{I_v}{I_r} = e^{-\pi \omega/kT} = 0.067$$
Thus

If the temperature is doubled, the rato increases to 0.259, an increase of 3.9 times.

#### Q.181. Consider the possible vibration modes in the following linear molecules: (a) $CO_2(O - C - O)$ ; (b) $C_2H_2$ (H--C - C--H).

#### **Ans.** (a) $CO_2(O - C - O)$

The molecule has 9 degrees of freedom 3 for each atom. This means that it can have up to nine frequencies. 3 degrees of freedom correspond to rigid translation, the frequency associated with this is zero as the potential energy of the system can not change under rigid translation. The P.E. will not change under rotations about axes passing through the C-atom and perpendicular to the O - C - O line. Thus there can be at most four non zero frequencies. We must look for modes different from the above.



One mode is



Another mode is

These are the only collinear modes.



A third mode is doubly degenerate :

(vibration in &  $\perp$  to the plane of paper).

(b) C<sub>2</sub>H<sub>2</sub> ( H - C - C - H )

There are  $4 \ge 3 - 3 - 2 = 7$  different vibrations. There are three collinear modes.



Two other doubly degenerate frequencies are



together with their counterparts in the plane  $\perp^r$  to the paper.

# Q.182. Find the number of natural transverse vibrations of a string of length l in the frequency interval from $\omega$ to $\omega + d\omega$ if the propagation velocity of vibrations is equal to v. All vibrations are supposed to occur in one plane.

Ans. Suppose the string is stretched along the x axis from x = 0 to x = 1 with the end points fixed. Suppose y(x, t) is the transverse displacement of the element at x at time t. Then y (x, t) obeys

$$\frac{\partial^2 y}{\partial t^2} = v^2 \frac{\partial^2 y}{\partial x^2}$$

We look for a stationary wave solution of this equation

$$y(x, t) = A \sin \frac{\omega}{v} x \sin (\omega t + \delta)$$

where A &  $\delta$  are constants.. In this from y = 0 at x = 0. The further condition

$$y = 0$$
 at  $x = 1$ 

implies  $\frac{\omega l}{v} = N\pi, N > 0$ 

Thus

or 
$$N = \frac{l}{\pi v} \omega$$

N is the number of modes of frequency  $\leq \omega$ .

$$dN = \frac{l}{\pi v} d\omega$$

Q.183. There is a square membrane of area S. Find the number of natural vibrations perpendicular to its plane in the frequency interval from  $\omega$  to  $\omega + d\omega$  if the propagation velocity of vibrations is equal to v.

Ans. Let  $\xi(x, y, t)$  be the displacement of the element at (x, y) at time t. Then it obeys the equation

$$\frac{\partial^2 \xi}{\partial t^2} = v^2 \left( \frac{\partial^2 \xi}{\partial x^2} + \frac{\partial^2 \xi}{\partial y^2} \right)$$

where  $\xi = 0$  at x = 0, x = l, y = 0 and y = l.

We look for a solution in the form

 $\xi = A \sin k_1 x \sin k_2 y \sin (\omega t + \delta)$ 

Then  $\omega^2 = \mathbf{v}^2 (k_1^2 + k_2^2)$ 

$$k_1 = \frac{n\pi}{l}, \ k_2 = \frac{m\pi}{l}$$

we write this as

$$n^2 + m^2 = \left(\frac{l\omega}{\pi v}\right)^2$$

Here n, m > 0. Each pair (n , m) determines a mode. The total number of modes whose frequency is  $\leq \omega$  is the area of the quadrant of a circle of radius  $\frac{l\omega}{\pi v}$  i.e.

$$N = \frac{\pi}{4} \left( \frac{l \,\omega}{\pi \, v} \right)^2$$
$$dN = \frac{l^2}{2 \pi v^2} \,\omega \, d\omega = \frac{S}{2 \pi v^2} \,\omega \, d\omega.$$
Then

where  $S = I^2$  is the area of the membrane.

# Q.184. Find the number of natural transverse vibrations of a right angled parallelepiped of volume V in the frequency interval from $\omega$ to $\omega + d\omega$ if the propagation velocity of vibrations is equal to v.

**Ans.** For transverse vibrations of a 3-dimensional continuum (in the form of a cube say) we have the equation

$$\frac{\partial^2 \vec{\xi}}{\partial t^2} = v^2 \vec{\nabla}^2 \vec{\xi}, \text{ div } \vec{\xi} = 0$$

Here  $\vec{\xi} - \vec{\xi}(x, y, z, t)$ . We look for solutions in the form

 $\vec{\xi} = \vec{A} \sin k_1 x, \sin k_2 y, \sin k_3 x, \sin (\omega t + \delta)$ 

This requires  $\omega^2 = \mathbf{v}^2 (k_1^2 + k_2^2 + k_3^2)$ 

From the boundary condition that  $\vec{\xi} = 0$  for x = 0, x = 1, y = 0, y = 1, z = 0, z = 1, we get

$$k_1 = \frac{n_1 \pi}{l}, \ k_2 = \frac{n_2 \pi}{l}, \ k_3 = \frac{n_3 \pi}{l}$$

where  $n_1$ ;  $n_2$ ,  $n_3$  are nonzero positive integers.

$$n_1^2 + n_2^2 + n_3^2 = \left(\frac{l\omega}{\pi v}\right)^2$$

We then get

Each triplet  $(n_1; n_2, n_3)$  determines a possible mode and the number of such modes whose frequency  $\leq \omega$  is the volume of the all positive octant of a sphere of radius  $\frac{l\omega}{\pi v}$ Considering also the fact that the subsidiary condition div  $\vec{\xi} = 0$  implies two independent values of  $\vec{A}$  for each choice of the wave vector  $(k_1, k_2, k_3)$ we find

$$N(\omega) = \frac{1}{8} \cdot \frac{4\pi}{3} \left( \frac{l\omega}{\pi v} \right)^3 \cdot 2 = \frac{V\omega^3}{3\pi^2 v^3}$$

Thus

$$dN = \frac{V\omega^2}{\pi^2 v^3} d\omega.$$

Q.185. Assuming the propagation velocities of longitudinal and transverse vibrations to be the same and equal to v, find the Debye temperature (a) for a unidimensional crystal, i.e. a chain of identical atoms, incorporating n<sub>o</sub> atoms per unit length;

(b) for a two-dimensional crystal, i.e. a plane square grid consisting of identical atoms, containing  $n_0$  atoms per unit area;

(c) for a simple cubic lattice consisting of identical atoms, containing  $n_{\scriptscriptstyle o}\,$  atoms per unit volume.

**Ans.** To determine the Debye temperature we cut off the high frequency modes in such a way as to get the total number of modes correctly.

(a) In a linear crystal with  $n_0$  atoms, the number of modes of transverse vibrations in any given plane cannot exceed  $n_0l$ . Then

$$n_0 l = \frac{l}{\pi v} \int_0^{\omega_0} d\omega = \frac{l}{\pi v} \omega_0$$

The cut off frequency  $\omega_0$  is related to the Debye temperature  $\bullet$  by

$$\hbar\,\omega_0\,=\,k\,\Theta$$

Thus  $\Theta = \left(\frac{\hbar}{k}\right) \pi n_0 \mathbf{v}$ 

(b) In a square lattice, the number of modes of transverse oscillations cannot exceed n<sub>o</sub>s.

Thus

$$n_0 S = \frac{S}{2 \pi v^2} \int_0^{\omega_0} \omega d\omega = \frac{S}{4 \pi v^2} \omega_0^2$$
  
$$\Theta = \frac{\hbar}{k} \omega_0 = \left(\frac{\hbar}{k}\right) \left(\sqrt{4 \pi n_0}\right) v$$
  
or

(c) In a cubic crystal, the maximum number of transverse waves must be  $2n_0 V$  (two for each atom). Thus

$$2 n_0 V = \frac{V}{\pi^2 v^3} \int_0^\infty \omega^2 d\omega = \frac{V \omega_0^3}{3 \pi^2 v^3}.$$
  
$$\Theta = \left(\frac{\hbar}{k}\right) v (6 \pi^2 n_0)^{1/3}.$$
  
Thus

Thus

#### **Molecules and Crystals (Part - 2)**

Q.186. Calculate the Debye temperature for iron in which the propagation velocities of longitudinal and transverse vibrations are equal to 5.85 and 3.23 km/s respectively.

**Ans.** We proceed as in the previous example. The total number of modes must be  $3n_0v$  (total transverse and one longitudinal per atom). On the other hand the number of transverse modes per unit frequency interval is given by

$$dN^{\perp} = \frac{V\omega^2}{\pi^2 v_{\perp}^3} d\omega$$

while the number of longitudinal modes per unit frequency interval is given by

$$dN^{\dagger} = \frac{V\omega^2}{2\pi^2 v_{\parallel}^3} d\omega$$

The total number per unit frequency interval is

$$dN = \frac{V\omega^2}{2\pi^2} \left( \frac{2}{\mathbf{v}_{\perp}^3} + \frac{1}{\mathbf{v}_{\parallel}^3} \right) d\omega$$

If the high frequency cut off is at  $\omega_0 = \frac{k \Theta}{\hbar}$ , the total number of modes will be

$$3 n_0 V = \frac{V}{6 \pi^2} \left( \frac{2}{v_\perp^3} + \frac{1}{v_\parallel^3} \right) \left( \frac{k \Theta}{\hbar} \right)^3$$

Here  $n_0$  is the number of iron atoms per unit volume. Thus

$$: \Theta = \frac{\hbar}{k} \left[ 18 \pi^2 n_0 / \left( \frac{2}{v_{\perp}^3} + \frac{1}{v_{\parallel}^3} \right) \right]^{1/3}$$

For iron

$$n_0 = N_A \left/ \frac{M}{\rho} = \frac{\rho N_A}{M} \right.$$

(p = density, M = atomic weight of iron  $N_A$  = Avogadro number).  $n_o = 8.389 \ x \ 10^{22} \ per \ cc$ Substituting the data we get

Θ = 469·1 K

## Q.187. Evaluate the propagation velocity of acoustic vibrations in aluminium whose Debye temperature is $\Theta = 396$ K.

Ans. We apply the same formula but assume  $v_{\parallel} = v_{\perp}$ . Then

]

$$\Theta = \frac{\hbar}{k} \mathbf{v} \left( 6 \pi^2 n_0 \right)^{1/3}$$
  
or  
$$\mathbf{v} = k \Theta / \left[ \hbar \left( 6 \pi^2 n_0 \right)^{1/3} \right]$$

For Al

$$n_0 = \frac{\rho N_A}{M} = 6.023 \times 10^{22} \,\mathrm{per \ c.c}$$

Thus v = 3.39 km/s.

The tabulated values are  $v_{\parallel} = 6.3 \text{ km/s}$ 

```
and v_{\perp} = 3.1 \text{ km/s}.
```

Q.188. Derive the formula expressing molar heat capacity of a unidimensional crystal, a chain of identical atoms, as a function of temperature T if the Debye temperature of the chain is equal to  $\Theta$ . Simplify the obtained expression for the case T >>  $\Theta$ .

**Ans.** In the Debye approximation the number of modes per unit frequency interval is given by

$$dN = \frac{l}{\pi v} d\omega \ 0 \le \omega \le \frac{k\Theta}{\hbar}$$
  
But 
$$\frac{k\Theta}{\hbar} = \pi n_0 v$$

Thus  $dN = \frac{l}{\pi v} d\omega, \ 0 \le \omega \le \pi n_0 v$ 

The energy per mode is  $\langle E \rangle = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\hbar \omega/kT} - 1}$ 

Then the total interval energy of the chain is

$$U = \frac{l}{\pi v} \int_{0}^{\pi n_{0}v} \frac{1}{2} \hbar \omega d \omega$$

$$+ \frac{l}{\pi v} \int_{0}^{\pi n_{0}v} \frac{\hbar \omega}{e^{\hbar \omega/KT} - 1} d\omega = \frac{l\hbar}{4\pi v} (\pi n_{0}v)^{2} + \frac{l}{\pi v \hbar} (kT)^{2} \int_{0}^{\infty} \frac{x \, dx}{e^{x} - 1} = l n_{0} k \cdot \frac{\hbar}{k} (\pi n_{0}v) \cdot \frac{1}{4}$$

$$+ l n_{0} k \frac{T^{2}}{(\pi n_{0}v \hbar/k)} \int_{0}^{\infty} \frac{x \, dx}{e^{x} - 1}$$

We put  $\ln_0 it = for 1$  mole of the chain.

$$U = R \Theta \left\{ \frac{\frac{\Theta}{T}}{\frac{1}{4} + \left(\frac{I}{\Theta}\right)^2} \int_{0}^{\infty} \frac{x \, dx}{e^x - 1} \right\}$$

Then

Hence the molar heat capacity is by differentiation

$$C_{V} = \left(\frac{\partial U}{\partial T}\right)_{\Theta} = R \left[ 2 \left(\frac{T}{\Theta}\right) \int_{0}^{\Theta/T} \frac{x \, dx}{e^{x} - 1} - \frac{\Theta/T}{e^{\Theta/T} - 1} \right]$$

when  $T >> \Theta$ ,  $C_v = R$ .

Q.189. In a chain of identical atoms the vibration frequency  $\omega$  depends on wave number k as  $\omega = \omega_{max} \sin (ka/2)$ , where  $\omega_{max}$  is the maximum vibration frequency, k =  $2\pi/\lambda$  is the wave number corresponding to frequency  $\omega$ , a is the distance between neighbouring atoms. Making use of this dispersion relation, find the dependence of the number of longitudinal vibrations per unit frequency interval on  $\omega$ , i.e. dN/d $\omega$ ,

### if the length of the chain is l Having obtained $dN/d\omega$ , find the total number N of possible longitudinal vibrations of the chain.

**Ans.** If the chain has N atoms, we can assume atom number 0 and N +1 held ficed. Then the displacement of the  $n^{th}$  atom has the form

$$u_n = A\left(\sin\frac{m\pi}{L} \cdot n\,a\right)\sin\omega\,t$$

Here  $k - \frac{m\pi}{L}$ . Allowed frequencies then have the form

$$\omega = \omega_{\max} \sin \frac{ka}{2}$$

In our form only +ve k values are allowed.

The number of modes in a wave number range dk is

$$dN = \frac{Ldk}{\pi} = \frac{L}{\pi} \frac{dk}{d\omega} d\omega$$

But

$$d\,\omega\,=\,\frac{a}{2}\,\omega_{\max}\,\cos\frac{k\,a}{2}\,d\,k$$

$$\frac{d\,\omega}{d\,k}=\frac{a}{2}\sqrt{\omega_{\rm max}^2-\omega^2}$$

Hence

$$dN = \frac{2L}{\pi a} \frac{d\omega}{\sqrt{\omega_{\max}^2 - \omega^2}}$$
So

(b) The total number of modes is

$$N = \int_{0}^{\omega_{max}} \frac{2L}{\pi a} \frac{d\omega}{\sqrt{\omega_{max}^2 - \omega^2}} = \frac{2L}{\pi a} \cdot \frac{\pi}{2} = \frac{L}{a}$$

i.e. the number of atoms in the chain.

## Q.190. Calculate the zero-point energy per one gram of copper whose Debye temperature is $\Theta = 330$ K.

Ans. Molar zero point energy is  $\frac{9}{8}R\Theta$ . The zero point energy per gm of copper

is  $\frac{9R\Theta}{8M_{C_{*}}}$ ,  $M_{C_{*}}$  is the atomic weight of the copper.

Substitution gives 48-6 J / g m .

Q.191. Fig. 6.10 shows heat capacity of a crystal vs temperature in terms of the Debye theory. Here  $C_{el}$  is classical heat capacity,  $\Theta$  is the Debye temperature. Using this plot, find:

(a) the Debye temperature for silver if at a temperature T = 65 K its molar heat capacity is equal to 15 J/(mol•K);

(b) the molar heat capacity of aluminium at T = 80 K if at T = 250 K it is equal to 22.4 J/(mol•K);

(c) the maximum vibration frequency for copper whose heat capacity at T = 125 K differs from the classical value by 25%



**Ans.** (a) By Dulong and Petit's law, the classical heat capacity is 3 R - 24-94 J/K - mole. Thus

$$\frac{C}{C_{Cl}} = 0.6014$$

From the graph we see that this

value of  $\frac{C}{C_{cl}}$  corresponds to  $\frac{T}{\Theta} = 0.29$ 

Hence  $\Theta = \frac{65}{0.29} = 224 \text{ K}$ (b) 22.4 J/mole - K corresponds to  $\frac{22\cdot4}{3\times8\cdot314} = 0.898$ .

From the graph this corresponds to

$$\frac{T}{\Theta} \sim 0.65$$
 This gives  $\Theta = \frac{250}{0.65} \sim 385$  K

Then 80 K corresponds to  $\frac{T}{\Theta}$  = 0.208

The corresponding value of  $\overline{c_{c_1}}$  is 0.42. Hence C = 10.5 J/mole - K.

(c) We calculate © from the datum tha  $\frac{c}{c_{cl}} = 0.75$  at T = 125 K.

The x-coordinate corresponding to 0.75 is 0.40. Hence

$$\Theta = \frac{125}{0.4} = 3125 \text{ K}$$

Now  $k\Theta = \hbar \omega_{max}$ 

So  $\omega_{max} = 4.09 \times 10^{13} \text{ rad/sec}$ 

Q.192. Demonstrate that molar heat capacity of a crystal at a temperature T <<  $\Theta$ , where  $\Theta$  is the Debye temperature, is defined by Eq. (6.4f).

**Ans.** We use the formula (6.4d)

$$U = 9R\Theta\left[\frac{1}{8} + \left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}\right]$$
  
=  $9R\Theta\left[\frac{1}{8} + \left\{\int_0^{\infty} \frac{x^3 dx}{e^x - 1}\right\} \left(\frac{T}{\Theta}\right)^4 - \left(\frac{T}{\Theta}\right)^4 \int_{\Theta/T}^{\infty} \frac{x^3 dx}{e^x - 1}\right]$ 

In the limit  $T << \Theta$ , the third term in the bracket is exponentially small together wil derivatives.

Then we can drop the last term

$$U = \text{Const} + \frac{9R}{\Theta^3} T^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

Thus

$$C_{V} = \left(\frac{\partial U}{\partial T}\right)_{V} = \left(\frac{\partial U}{\partial T}\right)_{\Theta} = 36 R \left(\frac{T}{\Theta}\right)^{3} \int_{0}^{\infty} \frac{x^{3} dx}{e^{x} - 1}$$

Now from the table in the book

$$\int_{0}^{\infty} \frac{x^3 \, dx}{e^x - 1} = \frac{\pi^4}{15}.$$

Thus 
$$C_v = \frac{12 \pi^4}{5} \left(\frac{T}{\Theta}\right)^3$$

Note Call the  $3^{rd}$  term in the bracket above -  $U_3$  Then

$$U_3 = \left(\frac{T}{\Theta}\right)^4 \int_{\Theta/T}^{\infty} \frac{x^3}{2\sin h (x/2)} \cdot e^{-x/2} dx$$

The maximum value of 
$$\frac{x^3}{2 \sin h \frac{x}{2}}$$
 is a finite + v e quantity C<sub>0</sub> for  $0 \le x < \infty$  Thus

$$U_3 \leq 2 C_0 \left(\frac{T}{\Theta}\right)^4 e^{-\Theta/2T}$$

$$T \rightarrow 0$$
. So is  $\frac{dU_3}{dT}$ 

we see that  $U_3$  is exponentially small as

### Q.193. Can one consider the temperatures 20 and 30 K as low for a crystal whose heat capacities at these temperatures are equal to 0.226 and 0.760 J/(mol- K)?

Ans. At low temperatures  $C \propto T^3$ . This is also a test of the "lowness" of the temperature We see that

$$\left(\frac{C_1}{C_2}\right)^{1/3} = 1.4982 \approx 1.5 = \frac{T_1}{T_2} = \frac{30}{20}$$

Thus  $T^3$  law is obeyed and  $T_1$ ,  $T_2$  can we regarded low .

# Q.194. Calculate the mean zero-point energy per one oscillator of a crystal in terms of the Debye theory if the Debye temperature of the crystal is equal to $\Theta$ .

Ans. The total zero point energy of 1 mole of the solid is  $\frac{9}{8}R\Theta$ . Dividing this by the

number of modes 3N we get the average zero point energy per mode. It is  $\frac{3}{8}k\Theta$ .

Q.195. Draw the vibration energy of a crystal as a function of frequency (neglecting the zero-point vibrations). Consider two cases:  $T = \frac{\Theta}{2}$  and  $T = \frac{\Theta}{4}$ , where  $\frac{\Theta}{4}$  is the Debye temperature.

Ans. In the Debye model

$$dN_{\omega} = A\omega^2, \ 0 \le \omega \le \omega_m$$

Then

 $3N - \int_{0}^{\pi} dN_{\omega} = \frac{A \omega_{m}^{3}}{3}.$  (Total no of modes is 3N)

 $A = \frac{9N}{\omega_m^3}.$ 

Thus

 $U = \frac{9N}{\omega_m^3} \int_0^{\omega_m} \frac{\omega^2 \cdot \hbar \omega}{e^{\hbar} \omega/k T - 1} d\omega$ ignoring zero point energy

wc get

$$= 9N\hbar\omega_{m}\int_{0}^{1} \frac{x^{3}dx}{e^{\hbar\omega_{m}x/kT}-1}, x = \frac{\omega}{\omega_{m}}$$

$$= 9R\Theta\int_{0}^{1} \frac{x^{3}dx}{e^{x\Theta/T}-1}, \Theta = \hbar\omega_{m}/k$$

$$= 9R\Theta\int_{0}^{1} \frac{x^{3}dx}{e^{x\Theta/T}-1}, \Theta = \hbar\omega_{m}/k$$

$$= \frac{1}{9R\Theta}\frac{dU(x)}{dx} = \frac{x^{3}}{e^{x\Theta/T}-1} \text{ for } 0 \le x \le 1$$
Thus

For

$$T = \Theta/2$$
, this is  $\frac{x^3}{e^{2x} - 1}$ ; for  
 $T = \frac{\Theta}{4}$ , it is  $\frac{x^3}{e^{4x} - 1}$  Plotting then we get the figures given in the answer.

### Q.196. Evaluate the maximum values of energy and momentum of a phonon (acoustie quantum) in copper whose Debye temperature is equal to 330 K.

Ans. The maximum energy of the phonon is

 $\hbar \omega_m = k\Theta = 28.4 \text{ meV}$ 

On substituting <sup>●</sup> - 330 K.

To get the corresponding value of the maximum momentum we must know the

dispersion relation  $\omega - \omega(\vec{k})$ . For small  $(\vec{k})$  we know  $\omega - v|\vec{k}|^2$  where v is velocity of sound in the crystal. For an order of magnitude estimate we continue to use this result for high  $|\vec{k}|$ . Then we estimate v from the values of the modulus of elasticity and density

$$v \sim \sqrt{\frac{E}{\rho}}$$

We write  $E \sim 100 \text{ GPa}$ ,  $\rho = 8.9 \times 10^3 \text{ kg/m}^3$ 

Then  $v \sim 3 \times 10^3 \text{ m/s}$ 

Hence  $\hbar |\vec{k}|_{\max} \sim \frac{\hbar \omega_m}{v} \sim 1.5 \times 10^{-19} \text{ gm cm s}^{-1}$ 

Q.197. Employing Eq. (6.4g), find at T = 0: (a) the maximum kinetic energy of free electrons in a metal if their concentration is equal to n;

(b) the mean kinetic energy of free electrons if their maximum kinetic energy T<sub>max</sub> is known.

Ans. (a) From the formula

$$dn = \frac{\sqrt{2} m^{3/2}}{\pi^2 \hbar^3} E^{1/2} dE$$

the maximum value  $E_{max}$  of E is determined in terms of n by

$$n = \frac{\sqrt{2} m^{3/2}}{\pi^2 \hbar^3} \int_0^{E} E^{1/2} dE$$
$$= \frac{\sqrt{2} m^{3/2}}{\pi^2 \hbar^3} \frac{2}{3} E_{\max}^{3/2}$$
$$E_{\max}^{3/2} = \left(\frac{\hbar^2}{2m}\right)^{3/2} (3\pi^2 n)$$

or

$$E_{\max} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

(b) Mean K.E.  $\langle E \rangle$  is

$$< E > - \int_{0}^{E_{max}} E \, dn \, / \int_{0}^{E_{max}} dn$$

$$-\int_{0}^{E_{\text{max}}} E^{3/2} dE / \int_{0}^{E^{1/2}} dE = \frac{2}{5} E_{\text{max}}^{5/2} / \frac{2}{3} E_{\text{max}}^{3/2} = \frac{3}{5} E_{\text{max}}$$

Q.198. What fraction (in per cent) of free electrons in a metal at T = 0 has a kinetic energy exceeding half the maximum energy?

Ans. The fraction is

$$\eta = \int_{\frac{1}{2}E_{max}}^{E_{max}} \frac{E_{max}}{e^{1/2}} dE / \int_{0}^{1/2} E^{1/2} dE = 1 - 2^{-3/2} = 0.646 \text{ or } 64.6\%$$

Q.199. Find the number of free electrons per one sodium atom at T = 0 if the Fermi level is equal to  $E_F = 3.07$  eV and the density of sodium is 0.97 g/cm<sup>3</sup>.

Ans. We calculate the concentration n of electron in the Na metal from

$$E_{\text{max}} = E_F = \frac{\hbar^2}{2 m} (3 \pi^2 n)^{2/3}$$

we get from

 $E_F = 3.07 \text{ eV}$   $n = 2.447 \times 10^{22} \text{ per c.c.}$ 

From this we get the number of electrons per one Na atom as

$$\frac{n}{\rho} \cdot \frac{M}{N_A}$$

where p = density of Na, M = molar weight in gm of Na,  $N_A = Avogadro$  number

we get

0.963 elecrons per one Na atom.

Q.200. Up to what temperature has one to heat classical electronic gas to make the mean energy of its electrons equal to that of free electrons in copper at T = 0? Only one free electron is supposed to correspond to each copper atom.

Ans. The mean K.E. of electrons in a Fermi gas is  $\frac{3}{5}E_F$ . This must equal  $\frac{3}{2}kT$ . Thus

$$T = \frac{2E_F}{5k}$$

We calculate  $E_F$  first For Cu

$$n = \frac{N_A}{M/\rho} = \frac{\rho N_A}{M} = "8.442 \times 10^{22} \text{ per c.c.}$$

Then  $E_{F=}$  7.01 eV

and T = 3 -2 5 x  $10^4$  K

#### Molecules and Crystals (Part - 3)

Q.201. Calculate the interval (in eV units) between neighbouring levels of free electrons in a metal at T = 0 near the Fermi level, if the concentration of free electrons is  $n = 2.0.10^{22}$  cm<sup>-3</sup> and the volume of the metal is V = 1.0 cm<sup>3</sup>

Ans. We write the expression for the number of electrons as

$$dN = \frac{V\sqrt{2} m^{3/2}}{\pi^2 \hbar^3} E^{1/2} dE$$

Hence if A  $\pounds$  is the spacing between neighbouring levels near the Fermi level we must have

$$2 = \frac{V \sqrt{2} m^{3/2}}{\pi^2 \hbar^3} E_F^{1/2} \Delta E$$

(2 on the RHS is to take care of both spins / electrons). Thus

$$\Delta E = \frac{\sqrt{2} \pi^2 \hbar^3}{V m^{3/2} E_F^{1/2}}$$

$$E_F^{1/2} = \frac{\hbar}{\sqrt{2} m^{1/2}} (3 \pi^2 n)^{1/3}$$
  
But

$$\Delta E = \frac{2 \pi^2 \hbar^2}{m \, V \, (3 \, \pi^2 \, n)^{1/3}}$$

Substituting the data we get

$$\Delta E = 1.79 \times 10^{-22} \, \text{eV}$$

Q.202. Making use of Eq. (6.4g), find at T = 0:
(a) the velocity distribution of free electrons;
(b) the ratio of the mean velocity of free electrons to their maximum velocity.

Ans. (a) From

$$dn(E) = \frac{\sqrt{2} m^{3/2}}{\pi^2 h^3} E^{1/2} dE$$

we get on using  $E = \frac{1}{2}mv^2$ , dn(E) = dn(v)

$$dn(\mathbf{v}) = \frac{\sqrt{2} m^{3/2}}{\pi^2 \hbar^3} \frac{1}{\sqrt{2}} m^{1/2} \mathbf{v} m \mathbf{v} d\mathbf{v} = \frac{m^3}{\pi^2 \hbar^3} \mathbf{v}^2 d\mathbf{v}$$

This holds for  $0 < v < v_F$  where  $\frac{1}{2}m v_F^2 - E_F$ 

and dn(v) = 0 for  $v > v_F$ .

(b) Mean velocity is

$$\langle \mathbf{v} \rangle = \int_{0}^{\mathbf{v}_{F}} \mathbf{v}^{3} d\mathbf{v} / \int_{0}^{\mathbf{v}_{F}} \mathbf{v}^{2} d\mathbf{v} = \frac{3}{4} \mathbf{v}_{F}$$
$$\therefore \frac{\langle \mathbf{v} \rangle}{\mathbf{v}_{F}} - \frac{3}{4}.$$

### Q.203. On the basis of Eq. (6.4g) find the number of free electrons in a metal at T = 0 as a function of de Broglie wavelengths

Ans. Using the formula of the previous section

$$dn(\mathbf{v}) = \frac{m^3}{\pi^2 \hbar^3} \mathbf{v}^2 d\mathbf{v}$$

We put  $mv = \frac{2\pi\hbar}{\lambda}$ , where  $\lambda =$  de Broglie wavelength

$$m\,d\,\mathbf{v}\,=\,-\frac{2\,\pi\hbar}{\lambda^2}\,d\,\lambda$$

Taking account of the fact that  $\lambda$  decreases when v increases we write

$$dn(\lambda) = -dn(\mathbf{v}) = \frac{(2\pi)^3 d\lambda}{\pi^2 \lambda^4} = \frac{8\pi}{\lambda^4} d\lambda$$

Q.204. Calculate the electronic gas pressure in metallic sodium, at T = 0, in which the concentration of free electrons is  $n = 2.5 \cdot 10^{22} \text{ cm}^{-3}$ . Use the equation for the pressure of ideal gas.

Ans. From the kinetic theory of gasses we know

$$p = \frac{2}{3} \frac{U}{V}$$

Here U is the total interval energy of the gas. This result is applicable to Fermi gas also Now at T = 0

$$U = U_0 = N < E > = nV < E >$$
  
SO  
$$P = \frac{2}{3}n < E >$$
$$= \frac{2}{3}n \times \frac{3}{5}E_F = \frac{2}{5}nE_F$$
$$= \frac{\hbar^2}{5m}(3\pi^2)^{2/3}n^{5/3}$$

Substituting the values we get  $p = 4.92 \text{ x } 10^4 \text{ atmos}$ 

Q.205. The increase in temperature of a cathode in electronic tube by  $\Delta T = 1.0$  K from the value T= 2000 K results in the increase of saturation current by  $\eta = 1.4\%$ . Find the work function of electron for the material of the cathode.

Ans. From Richardson's equation

$$I = a T^2 e^{-A/kT}$$

where A is the work function in eV. When T increases by  $\Delta T,$  I increases to  $(1+\eta)I.$  Then

$$1 + \eta = \left(\frac{T + \Delta T}{T}\right)^2 e^{-\frac{A}{kT}\left(\frac{T}{T + \Delta T} - 1\right)} = \left(1 + \frac{\Delta T}{T}\right)^2 e^{+\frac{A}{kT} \cdot \frac{\Delta T}{T + \Delta T}}$$

Expanding and neglecting higher powers of  $\frac{\Delta T}{T}$  we get

$$\eta = 2 \frac{\Delta T}{T} + \frac{A}{k T^2} \Delta T$$

$$A = kT \left(\frac{\eta T}{\Delta T} - 2\right)$$
Thus

Substituting we get A = 4.48 eV

Q.206. Find the refractive index of metallic sodium for electrons with kinetic energy T = 135 eV. Only one free electron is assumed to correspond to each sodium atom.

Ans.



The potential energy inside the metal is -  $U_0$  for the electron and it related to the work function A by

 $U_0 = E_p + A$ 

If T is the K.E. of electrons outside the metal, its K.E. inside the metal will be  $(E + U_0)$ . On entering the metal electron connot experience any tangential force so the tangential component of momentum is unchanged. Then

 $\sqrt{2 m T} \sin \alpha = \sqrt{2 m (T + U_0)} \sin \beta$ 

Hence

 $\frac{\sin \alpha}{\sin \beta} = \sqrt{1 + \frac{U_0}{T}} = n$  by the definition of refractive index

In sodium with one free electron per Na atom  $n = 2.54 \times 10^{22}$  per c.c.  $E_F = 3.15 \text{ eV}$  A = 2.27 eV (from table)  $U_0 = 5.42 \text{ eV}$ n = 102

#### Q.207. Find the minimum energy of electron-hole pair formation in an impurityfree semiconductor whose electric conductance increases $\eta = 5.0$ times when the temperature increases from $T_1 = 300$ K to $T_2 = 400$ K.

**Ans.** In a pure (intrinsic) semiconductor the conductivity is related to the temperature by the following formula very closely:

 $\sigma = \sigma_0 e^{-\Delta k/2kT}$ 

where  $\Delta \varepsilon$  is the energy gap between the top of valence band and the bottom of conduction band; it is also the minimum energy required for the formation of electronhole pair. The conductivity increases with temperature and we have

$$\eta = e^{i\frac{\Delta \varepsilon}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$
$$\ln \eta = \frac{\Delta \varepsilon}{2k}\frac{T_2 - T_1}{T_1 T_2}$$

U

$$\Delta \varepsilon = \frac{2 k T_1 T_2}{T_2 - T_1} \ln \eta$$

Hence

Substitution gives

 $\Delta \epsilon = 0.333 \, \text{eV} = E_{\text{min}}$ 

Q.208. At very low temperatures the photoelectric threshold short wavelength in an impurity-free germanium is equal to  $\lambda_{ih} = 1.7 \mu m$ . Find the temperature coefficient of resistance of this germanium sample at room temperature.

**Ans.** The photoelectric threshold determines the band gap  $\Delta \varepsilon$  by

$$\Delta \varepsilon = \frac{2 \pi \hbar c}{\lambda_{th}}$$

On the other hand the temperature coefficient of resistance is defined by (p is resistivity)

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT} = \frac{d}{dT} \ln \rho = -\frac{d}{dT} \ln \sigma$$

where  $\sigma$  is the conductivity. But

$$\ln \sigma = \ln \sigma_0 - \frac{\Delta \varepsilon}{2 \, k \, T}$$

$$\alpha = -\frac{\Delta \varepsilon}{2 \, k \, T^2} = -\frac{\pi \hbar c}{k \, T^2 \, \lambda_{th}} = -0.047 \, \mathrm{K}^{-1}$$
Then

Q.209. Fig. 6.11 illustrates logarithmic electric conductance as a function of reciprocal temperature (7' in kK units) for some



n-type semiconductor. Using this plot, find the width of the forbidden band of the semiconductor and the activation energy of donor levels.

**Ans.** At high temperatures (small values of  $T^{-1}$ ) most of the conductivity is intrinsic i.e. it is due to the transition of electrons from the upper levels of the valance band into the lower levels of conduction vands.

For this we can apply approximately the formula

$$\sigma = \sigma_0 \exp\left(-\frac{E_g}{2 k T}\right)$$

$$-\frac{1}{2 k T}$$
In  $\sigma = \ln \sigma_0 - \frac{E_g}{2 k t}$ 
or

From this we get the band gap

$$E_g = -2 k \frac{\Delta \ln \sigma}{\Delta (1/T)}$$

The slope must be calculated at small  $\frac{1}{\overline{r}}$ . Evaluation gives  $-\frac{\Delta \ln \sigma}{\Delta \left(\frac{1}{\overline{r}}\right)} = 7000 \text{ K}$ Hence  $E_g = 1.21 \text{ eV}$  At low temperatures (high values of  $\frac{1}{\overline{r}}$ ) the conductance is mostly due to impurities. If  $E_0$  is the ionization energy of donor levels then we can write the approximate formula (valid at low temperature)

$$\sigma' = \sigma'_0 \exp\left(-\frac{E_0}{2 k T}\right)$$
$$E_0 = -2 k T \frac{\Delta \ln \sigma'}{\Delta \left(\frac{4}{T}\right)}$$
So

The slope must be calculated at low temperatures. Evaluation gives the slope

$$-\frac{\Delta \ln \sigma'}{\Delta \left(\frac{1}{T}\right)} = \frac{\sqrt{1}}{3} \times 1000 \text{ K}$$

Then  $E_0 \sim 0.057 \, eV$ 

Q.210. The resistivity of an impurity-free semiconductor at room temperature is  $\rho = 50 \ \Omega \cdot cm$ . It becomes equal to  $\rho_i = 40 \ \Omega \cdot cm$  when the semiconductor is illuminated with light, and t = 8 ms after switching off the light source the resistivity becomes equal to  $\rho_2 = 45 \ \Omega \cdot cm$ . Find the mean lifetime of conduction electrons and holes.

Ans. We write the conductivity of the sample as

 $\sigma = \sigma_i + \sigma_\gamma$ 

where  $\sigma_i$  = intrinsic conductivity and  $\sigma_{\gamma}$  is the photo conductivity. At t = 0, assuming saturation we have

$$\frac{1}{\rho_1} = \frac{1}{\rho} + \sigma_{\gamma_0} \quad \text{ or } \quad \sigma_{\gamma_0} = \frac{1}{\rho_1} - \frac{1}{\rho}$$

Time t after light source is switched off we have because of recombination of electron and holes in the sample

$$\sigma = \sigma_i + \sigma_{\gamma_0} \ e^{-t/T}$$

where T = mean lifetime of electrons and holes.

 $\frac{1}{\rho_2} = \frac{1}{\rho} + \left(\frac{1}{\rho_1} - \frac{1}{\rho}\right) e^{-t/T}$ Thus  $\frac{1}{\rho_2} - \frac{1}{\rho} = \left(\frac{1}{\rho_1} - \frac{1}{\rho}\right) e^{-t/T}$ or  $e^{t/T} = \frac{\frac{1}{\rho_1} - \frac{1}{\rho}}{\frac{1}{\rho_2} - \frac{1}{\rho}} = \frac{\rho_2(\rho - \rho_1)}{\rho_1(\rho - \rho_2)}$ or  $T = t / \ln \left\{\frac{\rho_2(\rho - \rho_1)}{\rho_1(\rho - \rho_2)}\right\}$ Hence

Substitution gives  $T = 9.87 \text{ ms} - 0.01 \text{ sec}^2$ 

Q.211. In Hall effect measurements a plate of width h = 10 mm and length l = 50 mm made of p-type semiconductor was placed in a magnetic field with induction B = 5.0 kG. A potential difference V = 10 V was applied across the edges of the plate. In this case the Hall field is  $V_{\rm H}$ = 50 mV and resistivity  $\rho$  = 2.5  $\Omega$ •cm. Find the concentration of holes and hole mobility.

Ans.



We shall ignore minority carriers.

Drifting holes experience a sideways force in the magnetic field and react by setting up a Hall electric field  $E_{\gamma}$  to counterbalance it Thus

$$v_x B = E_y = \frac{V_H}{h}$$

If the concentration of carriers is n then

$$j_x = n e v_x$$

Hence 
$$n = \frac{J_x}{e v_x} = \frac{\frac{j_x}{e V_H}}{hB} = \frac{j_x hB}{e V_H}$$

$$j_x = \sigma E_x = E_x / \rho = \frac{V}{\rho l}$$

Also using

we get

$$n = \frac{VhB}{e\rho lV_H}$$

Substituting the data (note that in MKS units B=5.0~k~G=0.5~T)  $\rho=2.5~x~10^{-2}~ohm\text{-m}$  we get  $\qquad n=4.99~x~10^{21}~m^{-3}$ 

 $= 4.99 \text{ x } 10^{15} \text{ per cm}^{3}$ 

$$u_0 = \frac{v_x}{E_x} = \frac{V_H}{nB} \times \frac{l}{V} = \frac{V_H l}{hBV}$$

Also the mobility is

Substitution gives  $U_{\circ} = 0.05 \text{ m}^2/\text{ V}$  - s

Q.212. In Hall effect measurements in a magnetic field with induction B = 5.0 kG the transverse electric field strength in an impurity-free germanium turned out to be  $\eta = 10$  times less than the longitudinal electric field strength. Find the difference in the mobilities of conduction electrons and holes in the given semiconductor.

Ans.



If an electric Geld Ex is present in a sample containing equal amounts of both electrons and holes, the two drift in opposite directions.

In the presence of a magnetic field  $B_z = B$  they set up Hall voltages in opposite directions.

The net Hall electric field is given by

$$E_y = (v_x^* - v_x^-) B$$
$$= (u_0^+ u_0^-) E_x B$$
$$But \qquad \frac{E_y}{E_x} = \frac{1}{\eta} \text{ Hence}$$
$$|u_0^+ - u_0^-| = \frac{1}{\eta B}$$

Substitution gives  $|u_0^+ - u_0^-| = 0.2 \text{ m}^2/\text{volt} - \sec$ 

Q.213. The Hall effect turned out to be not observable in a semiconductor whose conduction electron mobility was  $\eta = 2.0$  times that of the hole mobility. Find the ratio of hole and conduction electron concentrations in that semiconductor

Ans.



When the sample contains unequal number of carriers of both types whose mobilities are different, static equilibrium (i.e. no transverse movement of either electron or holes) is impossible in a magnetic Geld. The transverse electric Geld acts differently on electrons and holes. If the  $E_y$  that is set up is as shown, the net Lorentz force per unit charge (effective transverse electric Geld) on electrons is

$$E_y - v_x^- B$$

and on holes

 $E_y + v_x^+ B$ 

(we are assuming  $B = B_z$ ). There is then a transverse drift of electrons and holes and the net transverse current must vanish in equilibrium. Using mobility

 $u_0^- N_e \, e \, (E_y - u_0^- E_x B \,) + N_k \, e \, u_0^+ \, (E_y + u_0^+ E_x B \,) \, = \, 0$ 

$$E_{y} = \frac{N_{e} u_{0}^{-2} - N u_{0}^{+2}}{N_{e} u_{0}^{-} + N_{h} u_{0}^{+}} E_{x} B$$

On the other hand

or

$$J_x = (N_e u_0^- + N_h u_0^+) e E_x$$

Thus, the Hall coefficient is

$$R_{H} = \frac{E_{y}}{j_{x}B} = \frac{1}{e} \frac{N_{e} u_{0}^{-2} - N_{h} u_{0}^{+2}}{(N_{e} u_{0}^{-} + N_{h} u_{0}^{+})^{2}}$$

We see that  $R_{\rm H} = 0$  when

$$\frac{N_e}{N_h} - \left(\frac{u_0^*}{u_0^*}\right)^2 - \frac{1}{\eta^2} - \frac{1}{4}$$