REGULAR CLASS

PG-TRB-ALL SUBJECT ADDMISSION GOING ON 21/04/2107,

PG-TRB-TAMIL, ENGLISH, ECONOMICS, PHYSICS, HISTORY,

MATHS, CHEMISTRY, BOTONY, ZOOLOGY, & COMMERCE

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PG TRB-PHYSICS- STUDY MATERIALS

UNIT-VII-FULL NOTES

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Solid State Physics:

Energy levels and density of states in one dimension:

Account of quantum theory

\[ E_n = \frac{n^2 \hbar^2}{2mL^2} \]

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

\( n \) = quantum number, \( m \) = mass of electron, \( L \) = box length.

Energy states depend on the KE and spin states of all constituent electrons.

Topmost filled level \( n = NF \), \( N \) is even.

Fermi energy \( E_F = \frac{\hbar^2}{2m} \left( \frac{N}{2L} \right)^2 \)

\[ N = 8 \text{ electrons} / \AA^2 \]

\[ E_F = \frac{\hbar^2}{2m} \left( 0.4 \right)^2 = 1 \text{ eV} \]

\[ E_0 = \frac{1}{3} N E_F \]

Average KE of ground state is one third of Fermi energy.

Density of states:

Density of states per unit energy range.

\[ \frac{2}{h^2} \frac{dn}{dE} = \frac{8 \pi^2 m}{\hbar^2} \frac{1}{n} \]

At filling energy, all other states are filled up to Fermi energy.

Free electron gas in three dimensions:

\[ E = \frac{\pi^2 \hbar^2}{2mL^2} n^2 \]

A is normalisation constant:

\[ A = \left( \frac{8}{5} \right)^{1/2} \]

Periodic boundary conditions for cyclic boundary conditions:

\[ k = \frac{2mE}{\hbar^2} = \frac{2\pi n}{\lambda} = \text{wave number} \]

\[ \mathbf{k} = \text{propagation vector} \]

\[ E_k = \left( \frac{\hbar^2}{2m} \right) k^2 = \frac{\hbar^2 k^2}{2m} \text{eV} \]

Fermi energy:

The level which divides filled and vacant levels is known as Fermi level at absolute zero. (E_F)

\[ E_F \approx 5 \text{eV} \]

but classical theory of electrons has a energy at absolute zero.

Density of states (r = \(\frac{1}{2}\)) is a parabolic function of energy for free electron gas in three dimensions.

Degree of degeneracy depends directly on the degree of symmetry of the system.
Filling up to energy level

\[ E(1, 1, 1) = \frac{3\hbar^2 \pi^2}{2mL^2} \]

\[ E(2, 1, 1) = \frac{6\hbar^2 \pi^2}{2mL^2} \]

The degeneracy of the last four states is three fold since the same energy value is obtained by three different quantum states.

Electrons occupy the state between 0 and \( \text{Ef}(0) \)

\[ \text{Ef}(0) = \frac{\hbar^2}{2m} \left( \frac{3n^2 \pi^2}{L^2} \right)^{3/2} \]

(by knowing electron concentration)

2. Electrical conductivity: \((\sigma)\)

Quantity of electricity that flows in unit time per unit area of cross-section of the conductor per unit potential gradient.

\[ \sigma = \frac{q}{A \text{E}} = \frac{i}{E} \]

\[ \sigma = \frac{ne^2 \lambda \sqrt{v}}{6k_BT} \]

Different \( \sigma \) of different materials due to different \( n \) of free electron

\[ \sigma \propto \frac{1}{T} \]

\[ \sigma = \frac{c^2 n m \times m s^{-1}}{J \text{K}^{-1} \text{K}^{-1}} = \frac{c^2 n m}{W} \]

\[ \sigma = \frac{eV}{F} \]

\[ \sigma = \frac{e^2}{c^2 W} \]

\[ W = qV \]

Thermal Conductivity:

\[
\frac{A}{T_2} > \frac{B}{T_r}
\]

Less energy goes.

More energy gets.

Kinetic theory of gases:

\[
E = \frac{3}{2} k_B T
\]

\[
Q = \frac{1}{2} n \nu A k_B \left( \frac{dT}{dx} \right) \rightarrow \text{a}
\]

\[
Q = k \frac{dT}{dx}
\]

\[
\text{compare } \text{(a) and (b)}
\]

\[
k = \frac{1}{2} n \nu A k_B
\]

\[
K = \text{thermal conductivity}
\]

\[
\frac{K}{\sigma} = LT \quad \text{units: } \text{Jm}^{-1} \text{K}^{-1}
\]

\[
\text{best electrical conductor: Ag, Cu, Al, Au}
\]

\[
\text{Widemann (1853) Franz ratio:}
\]

Thermal conductivity:

\[
\frac{K}{\sigma} = \text{electrical conductivity}
\]

\[
K = \text{constant for all metals (but not too low temp)}
\]

\[
\frac{k}{\sigma} = 3 \left( \frac{k_B}{e} \right)^2 T
\]

\[
\text{is independent of the nature of the metal and is proportional to absolute temp}
\]

\[
\text{Lenard-Zehnder:}
\]

\[
L = 2.44 \times 10^{-8} \text{ Wm} -2 \text{K}^{-2}
\]

\[
L = 2.93 \times 10^{-8} \text{ Wm} -2 \text{K}^{-2}
\]

\[
L = 2.44 \times 10^{-8} \text{ Wm} -2 \text{K}^{-2}
\]

\[
L = 2.93 \times 10^{-8} \text{ Wm} -2 \text{K}^{-2}
\]
Failure of the theory:

Free electron theory completely fails to explain the heat capacity and paramagnetic susceptibility of the conducting electron.

Energy bands in solids:

- The ng of holes in valence band equal to the ng of electrons in conduction band.
- Fermi level should be situated in the middle of the forbidden gap band (i.e., valence and conduction bands). The Fermi level is independent of temp.
- All valence electrons have an energy equal to or less than $E_v$ (Fermi energy).
- All conduction band electrons have energy equal to or greater than $E_c$.

Intrinsic semiconductor:
- Concentration of holes and electron must always be the same.

Extrinsic (or impurity) semiconductor:
- Concentration becomes unequal.

\[
\frac{V_d \times F}{V_d} = \mu F
\]

\[
\text{(IV) Mobility of electrons} = \frac{\text{Drift velocity}}{\text{Field Strength}} = \frac{ms^{-1}}{V \text{m}^{-1}} = m^2 V^{-1} \text{s}^{-1}
\]
Total conductivity

\[ \sigma = \sigma_n + \sigma_p \]

\[ = e \left( n \mu_n + p \mu_p \right) \]

(\text{He}) electron mobility at any temp will be different (greater) from the mobility of holes (\( \mu_p \)).

Conductivity of semi conductors increases with the rise in temp.

Electrons in \textit{Conduction band} may have energies lying from \( E_0 \) to \( \infty \). Electrons in \textit{Valence band} may have energies lying from \( -\infty \) to \( E_V \).

(i) In an \textit{Intrinsic} semi conductor, density of electrons in \textit{Conduction band} equal to density of holes in \textit{Valence band}.

(ii) \( n_e \) or \( n_h \) increase exponentially as the temp increases.

The mobilities \( \mu_n \) and \( \mu_p \) have a temp dependence and will largely cancel the \( T^{3/2} \)

\( \text{Energy gap for He} = 0.78 \text{ eV} \)

\( \text{Ei} = 1.21 \text{ eV} \)

\text{Law of Mass action:} The product of electron and hole concentrations for a given material constant at a given temp.
Donor impurity: pentavalent
Arsenic or antimony.

Acceptor impurity: trivalent
Boron or aluminium.

Density of electrons in the conduction band is proportional to square root of concentration.

The conductivity of intrinsic semiconductor is smaller than n or p type semiconductor

\[ P \propto \sqrt{\text{concentration}} \]

\[ \text{concentration} = \text{const} \times \text{holes} \times \text{electrons} \]
\[ \frac{V}{V_L} = \frac{N_d}{N_n} \]

\[ e = N_d x_2 - y_m \]

\[ C = \frac{e}{V} \]

\[ P = \frac{C}{V} \]
Operational functions of a junction diode:

- Charge depletion or space charge region
- No charge carriers
- Barrier voltage (01) contact potential

Charge density in p side of space charge region

\[ p = -eN_a \]

Potential distribution in space charge region

On 'n' side

\[ V_1 = -\frac{eN_a x_1^2}{2\varepsilon} \]

On 'p' side

\[ V_2 = \frac{eN_d x_2^2}{2\varepsilon} \]

Barrier width:

\[ x = \left( \frac{2\varepsilon V_2}{eN_a} \right)^{\frac{1}{2}} \]

Width of space charge region decreases as the impurity concentration increases.

\[ \frac{V_1}{V_2} = \frac{N_d}{N_a} \]

Nd - donor
Na - acceptor

Diode capacitance:

Total the charge in the n-type region is equal to

\[ \sigma = \frac{a}{x} \]

End \( x_2 \) c/cm²

the charge and -ve charge have equal magnitude.

Electron density in an extrinsic semiconductor depends on the Fermi level and addition of donor impurities. It simply increases Fermi factor

\[ \exp \left( \frac{E_F - E_C}{k_B T} \right) \]

Minority carrier density from the relation

\[ n_e n_h = n_i^2 \]

Barrier potential:

\[ V_B = \frac{e}{q} \log \left( \frac{n_d}{n_i^2} \right) \]

Note:
Density of electron in conduction band and of hole in VB = Boltzmann factor

\[ \exp \left( \frac{E_F - E_C}{k_B T} \right) \]

Electron current:

\[ I_{pn} = I_{np} = \text{Probability} \times \text{density of electrons in conduction band} \]

Peltier equation:

\[ I = I_0 \left[ \exp \left( \frac{eV}{k_B T} \right) - 1 \right] \]

Mobility of electrons:

\[ \mu = \frac{\sigma n}{e \nu} = \frac{\text{conductivity}}{\text{electric charge}} \]

\[ \frac{\Delta n}{\Delta t} = \frac{\mu}{\nu} \frac{\Delta V}{L} \]

\[ \frac{\Delta n}{\Delta t} = \frac{\mu}{\nu} \frac{\Delta V}{L} \]

Schottky effect:

Schottky emission is the combination of thermionic and field emission process. Schottky emission is also known as Schottky effect. It is possible to remove electrons from metal surface by the action of field. The field is very high. This is called field emission. The reflection or work function is known as Schottky effect. Image force is used in Schottky effect. Increase in electric field is called Schottky effect. Increase in electric field is called Schottky effect. The value is decreased. Work function is given by \( \Phi_F = 0 \). (Neglect field is strong)

Schottky diode is called hot carrier diode. Thermionic emission at constant temperature increases with applied field. Schottky effect is constant at higher temp.
Bloch Theorem:

Wave equation in a periodic potential.

Potential energy of the electron satisfies

the equation

\[ V(x) = V(x + a) \]

Bloch functions:

\[ \psi(x) = e^{\pm ikx} U_k(x) \]

\[ U_k(x) = U_k(x + a) \]

The solutions are plane waves, modulated

by the function \( U_k(x) \) which has the

same periodically as the lattice. This

Theorem is called Bloch Theorem.

- Bloch Theorem is a mathematical

statement regarding the form of the one

electron wave function for a perfectly

periodic potential.

1) Energy ranges in which \((\alpha_1 + \beta_2)^2 \leq 4\)

   - two roots will be complex.

2) Energy ranges in which \((\alpha_1 + \beta_2)^2 > 4\)

   - two roots are real.

There are no electronic states in this

region corresponding to real roots \( \lambda_1 \) and \( \lambda_2 \).

Periodic potential consists of allowed

and forbidden energy region.

The complex value of \( \mu \) corresponds

to allowed energy bands.

The real values of \( \mu \) corresponds

to forbidden energy band.
Kroning penny model:

- one of the simplest
- one dimensional periodic potential has been treated by Kroning penny
- highly artificial
- PE of an electron has the form of a periodic array of square wells
- It is obtained from the possible solution of Schrodinger’s equation
- Kroning Penny considered the case when \( V_0 \) tends to infinity and \( b \) approaches zero, but the product \( V_0 b \) remains finite.

\[ \frac{2}{2a} \sin \frac{\pi a}{2a} + \cos \frac{\pi a}{2a} = \cos \frac{\pi a}{2a} \]

\( da = \pm 1 \) in the second middle indicated by horizontal lines.

\[ E = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \]

Energy spectrum given as \( n = 0 \) or \( \infty \)

\( P = 0 \) (BE) \rightarrow \text{continuous parabola}

\( P = \infty \) \rightarrow \text{line spectrum} (\infty)\text{\textendash}\text{continuous}

Find out energy gap between the allowed values of energy of electron.
Allowed bands are narrower for low value of energy. The width of allowed bands decreases as energy increases. Unallowed bands get narrower.

Crs a is constant if \( k a \) is finite or \( xe \) increased by integer multiple of \( 2\pi \) but energy \( \frac{2\pi}{a} \)

Discontinuation of parabola

\[
k = \frac{n\pi}{a}
\]

Comparing \( nx = 2a \)

It is compared with Bragg diffraction. It is composed of Bragg diffraction depends upon energy well size and strength of diffraction leads to wider gaps.

Discontinuation at \( k = \frac{n\pi}{a} \): \( n = 1, 2, 3 \)

- \( k = \pi a \) to \( -\pi a \) first Brillouin zone.
- One from \( +\pi a \) to \( +2\pi a \) second Brillouin zone.
- Second \( -\pi a \) to \( -2\pi a \) second Brillouin zone.

Each position of the curve called a band.

(i) Horizontal at the top and bottom.
(ii) Parabolic near the top.
(iii) Curvature near the bottom in opposite direction.
(iv) \( \frac{d^2E}{dx^2} \) is the in lower portion of the band.
Bragg condition

\[(k + h)^2 = k^2 - \frac{1}{a^2}\]

\[h = \pm \frac{2\pi n}{a}\]  

**Reciprocal lattice vector**

(Three dimensional)

**Brillouin zones:** In (one dimensional) the energy discontinuity occurs when wave number \(k\) satisfies the condition \(k = \frac{n\pi}{a}\)

- **First zone** (smallest one)
- **Reduced zone**
- **Constructed from** the planes which are perpendicular to all reciprocal lattice vectors.

**Bragg’s equation:**

\[2k \cdot h + g^2 = 0\]

\(k = \) propagation vector = \(a\sqrt{3}\)

\(g = 2\pi h\) (times) the reciprocal lattice vector.

Each Brillouin zone for this lattice can be reduced into first zone.

- The shape becomes complex because additional Bragg reflections are obtained.

**Uses:**

- Theory of electronic bands in crystals.
- Theory of x-ray spectra.

**X-ray spectroscopy:** A set of planes and next set of planes.
Brillouin zones are volume contained in surface which indicate the forbidden values of \( k \) in momentum space.

Three dimensional representation in boundary of \( BZ \) zone dependent only on the periodicity from lattice points on the **periodicity** of the system.

(ii) Need reflecting planes for **cubic** not usually.

(iii) Define all possible \( k \) values are determined the single band.

(iv) Volume of \( BZ \) is states possible in a crystal lattice.

And its symmetry related to crystal lattice only geometry.

It can be used to determine the fermi surface (In it equal to fermi energy).

\[
\begin{align*}
W &= p dV \\
W &= F \times S \\
W &= p A \times S \\
W &= p V
\end{align*}
\]
Wave equation of an electron in a periodic potential:

1. No of possible wavefunction per band

\[ k = \frac{\pi n}{a} \quad (n = 1, 2, 3, \ldots) \]

No of possible wave \( \psi (x) \) \( k \) value

\[ \frac{dn}{dk} = \frac{1}{\pi a} \]

Maximum value of \( n \) given by

\[ \frac{L}{a^2} = \frac{N}{2} \]

- \( N \) = no of unit cells
- \( L \) = linear crystal length
- \( a \) = breadth

2. Total no of possible wavefunction in any energy band is equal to the no of unit cells \( N \)

\[ \frac{L}{a} = N \]

Group velocity \( v_g = \frac{d\omega}{dk} \)

\[ v_g = \frac{p}{m} = \frac{h k}{m} \]

Velocity of free electron \( v \sim k \)

Velocity of electron in zero at the bottom and top of the first Brillouin zone or band.

Slope is zero for \( k = 0 \) and \( k = \frac{\pi a}{a} \).
Intermediate region in the zone

to velocity or electron reaches to free electrons
velocity.

The absolute value of velocity reaches a maximum for $K = k_0$

where $K$ corresponds to be

inflection point of the $E(k)$ curve.

Beyond this point the velocity decreases with increasing energy.

Influence of electric field: $\frac{2mE}{h^2k}$

$k_0$ is called lattice momentum of the electron.

The motion of electron near the band edge is described by wave packet (or)
band edge, described wave packet (or) wavefunction.

Each has different wave

Chromatic wave.

The positive contribution to electron

The electron corresponds to zero velocity.

The electron does not obey Newtonian
equation in the region if momentum spike.

Whether the electron ever comes to the second Brillouin zone at all or not?

Yes, $k$ is slightly greater than $\pi$.

Bragg reflection and continues in backward motion.
Effective mass \( m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}} \)

At lower position \( E - K \) curve, \( \frac{d^2E}{dk^2} \) is +ve. Higher position, \( -ve \).

At the point of inflection, \( \frac{d^2E}{dk^2} = 0 \)

So, \( m^* = \infty \)

In \( E - K \) curve, \( K = 0 \), when an Elastic field is applied, the wave vector decreases linearly with time.

\[ f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \frac{d^2E}{dk^2} \]

The factor \( f_k \) determines the extent up to which the electron in a \( k \) state is a "free electron".

\( m^* \) large \( f_k \) is smaller.

If the particle behaves as a heavy particle

\( f_k = 1 \) electron behaves as a free electron.

There is why an electron remaining in one band can not go to another zone by applying a continuous force.

Consecutive Brillouin zones are separated by forbidden energy gap.
Thermal properties of Solid:

Laws of Thermodynamics:

Thermodynamics: Heat $\rightarrow$ Mechanical work

First Law:

$\Delta Q = \Delta U + \Delta W$

heat energy supply to the system =

Change in internal energy + work done by the system.

Isothermal Process: $P\ V$ = const

$T$ is constant.

Adiabatic Process: $P\ V^n$ = const

$T$ is variable.

T decreases adiabatic expansion
T increases adiabatic compression

$\gamma = \frac{C_p}{C_v}$ = Slope of adiabatic curve
$\delta = \frac{C_p}{C_v}$ = Slope of isothermal curve

$W = JQ$

$J = 4.2 \times 10^7$ erg/Cal.

1 Joule = 10$^7$ erg

1 Calorie = 4.2 Joule/Cal.

Spectrical motion machine of ice first kind is impossible.
Isobaric process - pressure constant

Isochoric process - volume constant
(non conductive)

Second law of thermodynamics:

Claussius statement: It is impossible for unaided...

Calvin statement: Cooling surrounding...

General statement:

Heat energy - work

Body kept at high temp - cool temp

Practical device - heat engines and refrigerators

Efficiency: \[ \eta = 1 - \frac{T_2}{T_1} \]

Heat energy converted into work

Heat energy drawn from its source

Change in entropy = \[ \frac{\text{Heat added or subtracted}}{\text{Absolute temp}} \]

\[ = J/k \text{ (01) cal/k} \]

Third law: \[ \frac{H_1}{T_1} = \frac{H_2}{T_2} \]

due to conduction, radiation & convection

\[ \frac{H_1}{T_1} - \frac{H_2}{T_2} \neq 0 \text{ but it is the quantity} \]
Second law

At absolute zero temp, the entropy tends to zero and the molecules of a substance or system are perfect order (well arranged).

Entropy is the measure of the disorder of the molecules of the system.

Maxwell's relation and their application:

Maxwell's relation:

Specification of certain quantities are

Pressure (P), Volume (V), Temp (T) & entropy (S)

which are independent variables.

I law of thermodynamics:

\[ dH = dU + dW \]
\[ dU = dH - dW \]
\[ dU = \delta H - p\delta V \]

II law

\[ dS = \frac{dH}{T} \]
\[ TdS = dH \]
\[ \therefore dH = TdS \]
First law: Internal or intrinsic energy

Internal energy is independent of the route followed between the two states.

\[ du = da - dw = T ds - pdV \]

\[ \frac{\partial T}{\partial V} s = -\left( \frac{\partial P}{\partial S} \right)_V \]

Second law: Helmholtz function (F)

F = U - TS

\[ F = \text{Helmholtz free energy (or) work function} \]

\[ \frac{\partial S}{\partial V} = \frac{\partial P}{\partial T} \]

Third law: Enthalpy or total heat (H)

\[ H = U + PV \]

\[ H - pV \text{ heat function (} dp = 0 \text{)} \]

For an isobaric process, change in enthalpy is equal to heat given to the system.

\[ dH = Tds + dQ \]

\[ \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \]
Fourth law: (Gibbs function)

\[
\begin{align*}
\theta &= H - TS \\
\theta &= F + PV
\end{align*}
\]

Thermodynamic potential at constant pressure (on Gibbs function)

The process is reversible if work done will be maximum (isothermal or isobaric)

The process is irreversible if work done will be less

\[
\frac{\partial V}{\partial T} = -\frac{\partial S}{\partial P}
\]

Maxwell's relation: (SPT + V)

As first numerator \( \frac{1}{2} \) in LHS

As second denominator \( \frac{3}{4} \) in RHS

\[
\begin{align*}
\frac{\partial S}{\partial V} &= \left(\frac{\partial P}{\partial T}\right) \\
\frac{\partial S}{\partial P} &= -\left(\frac{\partial V}{\partial T}\right) \\
\frac{\partial S}{\partial T} &= -\frac{\partial P}{\partial S} \\
\frac{\partial T}{\partial P} &= \frac{\partial V}{\partial S}
\end{align*}
\]
Application:

\[ \frac{dp}{dt} = \frac{L}{T} (V_2 - V_1) \]

Clapeyron-Clapeyron equation (latent heat)

2. Ratio of adiabatic and isothermal elasticities:

\[ \frac{\beta_s}{\beta_T} = \frac{E_s}{C_p} \frac{C_T}{C_v} \]

\[ B = \frac{E_s}{E_T} \]

Joule-Thomson coefficient for a perfect gas is zero:

\[ T_j = \frac{2a}{R_b} \]

Joule-Thomson expansion causes cooling effect, coefficient \( \mu = \left( \frac{\partial T}{\partial p} \right)_T \)

Adiabatic stretching of wire:

\[ \frac{dT}{df} = \frac{-T_B}{mc} df \]

If \( \beta \) is positive, an increase in tension would cool the wire.

Wire of substance which expand on heating should show a cooling when stretched adiabatically.

Change of temp during adiabatic process:

- Compression: temp increase
- Expansion: temp decrease

Show that:

1. \( c_p - c_v = T E_a^2 V \)

2. \( \frac{E_s}{E_t} = \frac{c_p}{c_v} = \gamma \)

3. \( c_2 - c_1 = \frac{dL}{dT} - \frac{L}{L} \)

4. Specific Heat at Saturated Steam

5. \( \frac{\partial s}{\partial p} = \frac{1}{1 - \frac{\gamma}{\gamma - 1}} \)

6. \( \frac{\beta s}{\beta V} = \frac{\gamma}{\gamma - 1} \)

For a perfect gas:

\( \left( \frac{\partial u}{\partial T} \right)_V = 0 \)

Bose gas does not show any change in temp.

\( \alpha = \frac{p - \rho}{\rho} \)

\( \beta = \frac{\rho - \rho}{\rho} \)
Phase transition: (Hibbs)

As the change takes place at constant temperature (isothermal) and constant pressure (isobaric),

\[ \Delta G = 0 \]

Specific gibbs potential \( \delta_1, \delta_2 \)

At phase transition

\[ \delta_1 = \delta_2 \rightarrow 0 \]

The thermodynamical potential for unit mass will be equal in two phases.

Eqn \( \delta \) applicable to the process of evaporation, fusion, and sublimation.

1. First order phase transition,

An enclosure containing a liquid and its saturated vapour in equilibrium undergoes an isothermal, isobaric change.

If the temperature increases, saturation takes place

\[ \left( \frac{d\delta_1}{dT} \right)_{\text{sat}} = \left( \frac{d\delta_2}{dT} \right)_{\text{sat}} \]

\[ S_2 - S_1 = \frac{\Delta H}{T} = \frac{L}{T} \]

(26) Latent heat of vapourisation

\[ \frac{dp}{dT} = \frac{L}{T (V_2 - V_1)} \]

Clapeyron latent heat equation

This equation holds good in first order phase transition. In this process, transference of heat and change in entropy and volume.

\[ \Delta G = \Delta H - T \Delta S \]

In order transition, defined Gibb's to wits with respect to pressure and temp change discontinuous at its transition point.

Gibbs free in same symbol as phase equilibrium:

\[ (G_1 = G_2) \]

Note: Gibbs function also known as thermo dynamical potential.

Gibbs free in latent energy

\[ \Delta G = \Delta H - T \Delta S \]
\[ \Delta G = u + pV - T S \]

\[ \text{Constant or sublimation and transmogrification and evaporation} \]

(ii) Second order phase transition. (See distinguish)

Example:
1. He I to He II
2. Ferro to para
3. Super conductor - conductor (Mag field = 0)
4. Order disorder in chemical compounds and alloys (check old).
First order phase transition

Transference of heat and change in volume and entropy.

\[ \frac{dp}{dt} = \frac{1}{T} \frac{(V_2 - V_1)}{\Delta s} \] (Clausius-Clapeyron Latent Heat equation)

Energetics equation

Second order phase transition

No transference of heat and no change in volume

No change in entropy and volume at constant temp and pressure.

\[ \frac{dp}{dt} = \frac{\Delta s - \Delta V}{k_2 - k_1} \] (Second order phase transition)

\[ \frac{V_1}{V_2} \]

Production and measurement of very low temperature: intimately linked with liquefaction of gases.

Methods:

1. Refrigerator: Coefficient of Performance (COP) \[ \beta = \frac{T_2}{T_1 - T_2} \]

\[ \beta \approx 2 \text{ to } 6 \]

\[ \eta = \frac{1 - \beta}{\beta} \]
2. Adding salt to ice: freezing mixture.
   Minimum temp - (eutectic temp)

3. Cooling by evaporation of liquid under reduced pressure.
   Ex: \( \text{NH}_3, \text{SO}_2 \)

   Vapour compression machine:
   \[ \beta = \frac{H_b - H_a}{H_c - H_b} = \frac{\Delta Q_2}{W} \]

4. Adiabatic expansion:
   Gas expansion machine
   \[ \beta = \frac{\Delta Q_2}{W} = \frac{\Delta Q_2}{Q_1 - Q_2} \]

5. Joules Thomeon expansion:
   (CO) Adiabatic throttling
   The temp above to temp of inversion
   The gas show heating effect

6. Regenerative cooling:
   Process used to cool a gas continuously is called regenerative cooling.
   Efficiency \( X = \frac{H_f - H_e}{H_f - H_i} \)

7. Adiabatic demagnetisation of a paramagnetic salt:
   Salt, susceptibility \( \chi \) is small but the
   \( \text{Debye 1926} \)
Paramagnetic salt - Gadolinium sulphate

temp below 1 K

Hass 1941 - double sulphate of potassium and aluminium

Curie temp

\[ T^* = \frac{C}{y} \]

magnetic temp

\[ T^* = 0.003 K \]

Note:

(i) \( \text{CO}_2 \) liquefies only at temp below 31.1°C (at critical temp)

(ii) \( Ti = 6.75 Tc \) (Tc - critical temp)

(iii) \( Ti = 2T_b \) (Tb - boiling point)

(iv) \( Ti \text{ for actual gas in just less than } Tc \)

\[ Ti = 2T_b = 6.75 Tc \]

\[ Ti > T_b > Tc \]

(iv) Liquefaction of air - Linde's process, Clait

(v) Liquefaction of Hg - Dewar & Carade process

He has no triple point

He II is called super fluid
1) The vapour pressure thermometer up to \( \pm 1\% \\
2) Liquid thermometer with \( \text{CH}_4 \) accuracy \( 0.1^\circ C \) up to \(-112^\circ C \\
3) Gas thermometer with \( \text{He} \) up to \(-253^\circ C \\
\text{with He} \quad -268.7^\circ C \\
4) Resistance thermometer with \( \text{Pt} \) accuracy \( 0.01^\circ C \) up to \(-100^\circ C \) to \(-190^\circ C \\
\text{Recently with carbon} \quad \text{to below} \ 1^\circ C \\
5) Thermo electric thermometer with \( \text{Cu} - \text{Pt} - \text{Ag} \) up to \(-255^\circ C \) accuracy \( 0.5^\circ C \\
6) Vapour pressure thermometer with \( \text{He} \) with water vapor up to \(-268^\circ C \\
-272^\circ C
Einstein & Debye theory of specific heats.

Dulong Petit's law:

The product of atomic weight and the specific heat (atomic heat) of an element at constant volume is constant for a number of elements in solid state equal to \( 5.96 \). Atomic heat = \( \frac{\text{atomic weight}}{\text{specific heat}} \).

\[
SR = 3 \times 1.9856 \\
= 5.9488
\]

It is derived from kinetic molecular theory.

Einstein theory of specific heat:

1906 - by the basis of quantum theory:

- Atoms are rest at 0K, so thermal kinetic energy is 0.
- All the atoms are vibrate at the same freq. (natural freq.)
- Each atom has three degrees of freedom.
- Mean energy / degree of freedom: \( \frac{h \nu}{e^{\frac{h \nu}{kT}} - 1} \).
\[ C_v = 3R \left( \frac{\Theta}{e^{\Theta/T} - 1} \right)^2 \]
\[ \Theta = \frac{h\nu}{k} \]

**Merit:**
\[ T = 0 \quad C_v = 0 \]

1. So atomic heat capacity decreases with decrease of temp
2. At high temp atomic heat \( (C_v) \) approaches \( 3R \). \( \text{(approx 6)} \)
\[ R = 1.95 \]
3. At low temp lattice specific heat proportional to \( T^3 \) law
4. All oscillators are in state of zero point energy.
\[ (\frac{1}{2} h\nu) \]

Specific heat of quantum oscillator will be less than classical oscillator.

**Debye theory of specific heat:**

- Vibrate independently at the same freq, oscillators are coupled together.
- Oscillators are capable of producing spectrum of free mass points.
- Vibration models of a crystal as a whole (but Einstein vs Debye).

- Einstein individual.
- Debye specific heat for whole.
Continuous solid is subjected to elastic vibrations. Two kinds of vibrations:

- Transverse vibration
- Longitudinal vibration

\[ f \left( \frac{c}{T} \right) = \text{Debye function, very rapidly with increasing freq.} \]

\[ \Theta = \frac{h \nu}{K} = \text{Debye temp.} \]

Merlin:

1. At high temp \( C_v = 3R \)

\[ C_v = \frac{3\nu k_b}{T} \text{ with decrease in temp.} \]

At low temp:

\[ C_v = \begin{cases} \frac{3}{2} k_b & T \to 0 \\
\left( C_v \times T^3 \right) & \text{otherwise} \end{cases} \]

- At low temp: Phonons and Phonons

\[ E \propto T^4 \]

T^4 law

But phonons obey T^4 law at all temp.

The specific heat capacity by Debye's law is

1. Proportional to the cube of the absolute temp. at low temp.

\[ C_v \propto T^3 \]

C2 constant at high temp.

C3 equal to 3R at high temp.

\[ \frac{13}{12} \text{ sec} \text{ to sec} \text{ per sec.} \]

Debye's cut off wave order = \( C_0 \text{ cm}^{-1} \text{ at } 700 \text{ K} \)

Debye's cut off wave order may be at the boundary. But the continuum theory may be at small wave numbers.

\[ \lambda \approx \frac{1}{\Theta} \]

Magnetic properties of materials

Langevin's theory of diamagnetism

- basis of Curie Law (curve equation result)
- Diamagnetic material real susceptibility

is independent of temp and field strength

depends on mass

Magnetic moment \[ M = iA \]

= current \times area

= \left( \frac{eW}{2\pi} \right) \pi r^2 = \frac{e}{2} \omega r^2

Additional force (or) Lorentz force

\[ F_L = -e(v \times B) = -eBrw \cdot \omega \]

Larmor's theorem

\[-(e/2m)vB \]

Induced magnetic moment is opposite to that of field

Susceptibility is determined essentially by the charge distribution in the atoms.

The phenomenon of diamagnetism is a result of magnetic dipole moment formation due to the presence of an external magnetic field.
Langevin theory of paramagnetism:

paramagnetic gas in which each atom or molecule possesses a permanent magnetic moment.

The mutual magnetic interaction between the different gas particles is neglected.

\[ M = m n L(\alpha) \]

\[ L(\alpha) = \left( \coth \alpha - \frac{1}{\alpha} \right) \]

\[ \mu = \mu L(\alpha) \]

\[ M = n m \frac{x}{3} \]

\[ Q = \frac{M}{H} = \left( \frac{\mu_0 n m^2}{3 k} \right) T = \frac{C}{T} \]

\[ C = \frac{\mu_0 n m^2}{3 k} \]

\( x = \frac{\mu H}{k_B T} \)

At low temp (or) large applied field: \( L(\alpha) \rightarrow 1 \)

\( M = n n \frac{x}{3} \)

\( x \) is very small: \( M < n m \)

1. **Bohr magnetron** \( \propto 10^{-20} \text{ erg/gas} \)

\[ \psi = \frac{\text{constant}}{T} \]

**Failure:**
- Unable to explain \( \psi \) of highly compressed, and cooled gases and concentrated solutions of salts.
- Only explain gas not solid, liquid.
- Could not account for the intimate relation between para and ferro magnetism.

2. **Weiss modification**

\[ \gamma = \frac{C}{T-\Theta} \]

\( \Theta \) - Curie temp.

**Diamagnetism examples:**
- S, Bi, Zn, Ag, Au, Pb

**Para magnetism**
- Mn, Cu, Ca, Al, Pt liquid viscosity
- Solution of Fe and Ni salts, crown gases

**Ferro magnetism**

\( \chi = \frac{\mu H}{K_B T} \)

- **Case 1**
  \( \mu H > K_BT \)
  \( L(\alpha) = 1 \)
  \( \alpha \text{ small } H \text{ large} \)
- **Case 2**
  \( \mu H < K_BT \)
  \( L(\alpha) = \alpha \beta \)
  \( \alpha \text{ small } H \text{ large} \)
Quantum theory of paramagnetism

If can be only certain permitted orientation of electronic orbit (or atom).

\[ \cos \theta = \frac{M_J}{J} \]

\( J \) - resultant spin no

\( M_J = (2J + 1) \) possible values: \( J, J-1 \)...

The component to \( H \) is equal to \( M_J / g \mu_B \)

\( g \) - Lande splitting factor

\[ \mu = \frac{g}{m} \mu_B \]

\( \chi = \frac{M_J}{H} \) or applied field \( H \).

\[ T \delta \frac{1}{h} \]

\( \mu_H = g \sqrt{J(J+1)} \)

Effective no of Bohr magneton.

(a) When the energy of transition between two states is very large compared to \( k_B T \) called wide multiplet.

(b) When the energy of transition between two states is very small compared to \( k_B T \) called narrow multiplet.
All spins (or) magnetic moments are randomly oriented.

Paramagnetic Curie temp is very low i.e. 100 K.

Note: Paramagnetic cooling or adiabatic demagnetisation used to idea of a tensile final temp obtained by cooling process.

Ferromagnetism:

\[ \lambda = \text{weiss constant} \]

\[ H_i \propto M \]

\[ H_i = \chi M \]

Slope of every line is proportional to the corresponding value of temp 'T'.

\[ \Theta \propto \lambda \]

\[ J = \infty, 1, \frac{1}{2} \]

Curves are closely e-magnetisation of ferromagnetic material arises due to electron spin rather than due to orbital motion.

Its magnetisation 16 times more than that of para.

\[ \frac{\gamma}{T} = \frac{c}{T_0} \]
1. Ferromagnetic materials

- Anti-ferrite
- Ferrite

- Ferrimagnetism: it is a special case of anti-ferrite magnetism.

$$\uparrow \uparrow + \downarrow = \uparrow, \quad \uparrow \downarrow = \uparrow$$

A kind of ferro magnetism as a result of antiferromagnetic coupling and is termed as ferrimagnetism by Neel temperature.

- Garnets: $\text{Mg}_3 \text{Fe}_5 \text{O}_{12}$ (Neel temperature)
- Yttrium iron garnet: $\text{Y}_3 \text{Fe}_5 \text{O}_{12}$, called $\text{YIG}$

- The magnetic moment per unit formula ($\text{Y}_3 \text{Fe}_5 \text{O}_{12}$) is that of one $\text{Fe}^{3+}$ ion and is equal to $5 \mu_B$.

- Given by Geller

- Magnetic moment of two sub-lattices are not equal in magnitude because of difference in number of atomic dipoles or nature of atoms.

- Mott's antiferromagnetic theory: verified Heisenberg model of $\text{Fe}_2 \text{O}_3$.

- Resistivity $\rho = \frac{1}{2} \frac{\text{Ohm}}{\text{cm}}$ (Comparison: $\text{Fe}_2 \text{O}_3$ has high $\rho$).
Superconductivity:

The temperature at which the resistance disappears in zero magnetic field is called transition temp.

Transition temp range of about 0.05°C

Various metals

1 to nearly 19 K (23.2 K)
0.01 K for tungsten
0.01 K for germanium

* Na and K super conductor $T_c$ is

less than $10^{-5}$ K

* Super conductivity is absent in ferro, monovalent metals, rare earth element (except lanthanum)

Resistivity of metal $e = \frac{m}{n e^2 r}$

$T \to \infty \quad \rho \to 0$

Super conducting transition is reversible

Effect of magnetic field

The critical field

$H_c = H_0 \left(1 - \frac{T^2}{T_c^2}\right)$

$T = T_c \quad H_c = 0$

Superconducting properties of metals can be changed by varying temp, magnetic field, magnetic trap of excitation.
Type 1: Super conductors or soft superconductors

Type 2: "" hard ""

Type 1: Al Zn Rha

Type 2: Zr Ni (Produce 100 keV)

Ni Curie temp: 258°C

Magnetic properties of super conductors:

- Magnetic properties of super conductors:
  - Perfect diamagnetism or Meissner effect
  - The Meissner effect occurs in Type I superconductors

The expulsion of magnetic flux from the interior of a piece of superconducting material as the material undergoes the transition to the superconducting phase is known as the Meissner effect.

Meissner effect:

Maxwell equation: \( B = \text{constant} \)
\[ B = H + 4\pi I \]  \( \text{Eq} \) 3

\[ B = 0, \quad H = -4\pi I \]

\[ k = \frac{I}{H} = -\frac{1}{4\pi I} = -\frac{1}{4\pi} \]

\[ E = 0 \quad \text{from the absence of relativity} \]

\[ B = 0 \quad \text{from the Meissner effect} \]

**Penetration depth (\( \lambda \))**

\[ \lambda = \frac{m}{\kappa_0 n e^2} \]

- \( m \): mass
- \( e \): charge of electron
- \( n \): no. of superconducting electrons/\( \text{unit vol} \)

**Penetration depth**

\( \lambda \) varies between 200 to 5000 \( \text{Å} \)

\( \lambda \) much greater than atomic distance

**Effect of heavy current**

- Gilbee's rule
- \( I_c = 2\pi r H_c \)

**Pressure:**

\[ T_c \propto d^{-1/2} \] \text{at high pressure}.

**Isotope effect:**

\[ T_c \propto \frac{1}{\sqrt{M}} \]

\[ M^2 T_c = \text{constant} \]

\[ T_c = 4.185 \text{ to } 4.186 \text{ K} \]

\[ M = 199.5 \text{ to } 203.4 \text{ amu} \]