Unit – 7 (B)
Solid state Physics

Thermal Properties of solids:

Zeroth law of Thermodynamics: If two bodies A and B are each separated in thermal equilibrium with the third body C, then A and B are also in thermal equilibrium.

First law of thermodynamics: It is also called the law of conservation of energy. The law states that, the amount of heat supplied to a system is equal to the algebraic sum of the change in the internal energy of the system and the amount of external work done by the system.
\[ dQ = du + dw \]

Second law of thermodynamics:

1) By Kelvin statement:
   It is impossible to obtain a continuous supply of work from a body by cooling it to a temperature lower than that of the surroundings.

2) By classius statement:
   It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the substance.

Efficiency \( (\eta) \) = \( \frac{\text{Amount of heat converted into work}}{\text{Total heat absorbed}} \)
\[ \eta = \frac{H_1 - H_2}{h_1} = 1 - \frac{H_2}{h_1} \text{ or } \]
\[ \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \text{ or } \]
\[ \eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \text{ or } \]

The second law of thermodynamics gives the condition under which heat can be converted into work. Carnot’s Engine is based on the above concept.

Carnot’s Theorem:
All reversible heat engines working between the same two temperature limits have the same efficiency. No engine can be more efficient than a Carnot’s reversible engine working between the same two temperatures.

All reversible heat engines have more carnot engint has maximum efficiency. So carnot engine is a reversible one.

Eg:- Find the efficiency of a carnots engine working between 127°C and 27°C
\[ T_1 = 273 + 127 = 400 \text{ K} \]
\[ T_2 = 273 + 27 = 300 \text{ K} \]
\[ \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25 \text{ K} \]

\[ \therefore \text{% of efficiency} = 25\% \]

Find the efficiency of the Carnot engine working between the steam point and the ice point.

\[ T_1 = 273 + 100 = 373 \text{ K} \]

\[ T_2 = 273 + 0 = 273 \text{ K} \]

\[ \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{100}{373} \]

\[ \% \text{ of efficiency} = \frac{100}{373} \times 100 = 26.81\% \]

**Entropy**: It is a thermodynamical property and is defined by the relation.

\[ ds = \frac{\delta Q}{T} \quad \text{(or)} \]

\[ S_1 - S_2 = \int_1^2 \frac{\delta Q}{T} \]

The entropy remains constant during an adiabatic process. When heat is absorbed during a process, there is increase in entropy and when heat is rejected during a process there is decrease in entropy.

* The unit of entropy is Joule/K or K cal/K
* From the relation, \( \delta S = \frac{\delta Q}{T} \)
* \( \delta Q \) – Heat added or subtracted
* \( T \) – Absolute Temperature
* Total change in entropy in a reversible cycle is zero (Carnot’s cycle)
* Entropy of a system increases in all irreversible processes.

![Image of a phase diagram showing the states of a substance with changes in entropy](http://www.trbtpsc.com/2013/07/trb-questions-and-study-materials.html)
Third law of Thermodynamics: (Nernst Heat Theorem)

A absolute zero temperature the entropy tends to zero and the molecules of a substance or a system are in perfect order (well arranges)

* Entropy is a measure of disorder of molecules of the system.
* Zero point energy: The energy of the molecules at absolute zero temperature is called zero point energy.
* With the decrease in entropy, the disorder decreases.

Extensive variables depends upon the mass or size of the substance.

Eg: Mass, volume, entropy, length, area, electric charge.

Intensive variables are independent of mass or size of the system.

Eg: Pressure, temp, viscosity, density emf, surface tension.

Maxwell’s Thermodynamical relations.

From the 2 laws, by Thermodynamics, Maxwell was able to derive 6 fundamental thermodynamical relations. The state can be specified by any pair of quantities.

* Pressure (P) * Volume (V) → PV Mechanical
* Temperature (T) * Entropy (S) → Thermal (TS)

From the I law of thermodynamics,

\[ \delta Q = du + \delta w \]

From II law of thermodynamics,

\[ \delta S = \frac{dQ}{T} \]

Using I law

\[ \delta Q = du + \delta w \] (or)
\[ \delta Q = du + Pdv \] (or)

\[ du = \delta q - P \frac{dv}{T} \] \hspace{1cm} \text{(1)}

Using II law,

\[ \delta S = \frac{dQ}{T} \]

\[ \delta q = T \delta s \] \hspace{1cm} \text{(2)}

Equation (3) is combination of (1) & (2)

\[ \left( \frac{\partial T}{\partial y} \right)_{x} \delta y \cdot \left( \frac{\partial P}{\partial x} \right)_{y} \delta x = \left( \frac{\partial V}{\partial x} \right)_{y} \delta y \cdot \left( \frac{\partial S}{\partial y} \right)_{x} - \left( \frac{\partial P}{\partial x} \right)_{y} \delta x \cdot \left( \frac{\partial V}{\partial y} \right)_{x} \]

This is the general expression for Maxwell’s thermo dynamical relation,

**Maxwell’s I thermodynamical relation:-**

Put \( x = S \) and \( Y = V \)

\[ \frac{\partial S}{\partial x} = 1 ; \frac{\partial v}{\partial y} = 1 \Rightarrow \delta S = \delta x ; \delta v = \delta y \]

\[ \left( \frac{\partial T}{\partial y} \right)_{x} = - \left( \frac{\partial P}{\partial x} \right)_{y} \]

\[ \left( \frac{\partial T}{\partial S} \right)_{v} = \frac{\partial P}{\partial S} \]

Maxwell’s I thermodynamical relation.
Maxwell’s II thermodynamic relation
Put \( x = T \) and \( y = V \)
\[
\frac{\partial T}{\partial x} = 1 ; \quad \frac{\partial V}{\partial y} = 1 \Rightarrow \partial x = \partial T ; \quad \partial y = \partial V
\]
\[
\frac{\partial T}{\partial y} = 0 ; \quad \frac{\partial V}{\partial x} = 0
\]
\[
\therefore (0)_T \left( \frac{\partial S}{\partial T} \right)_V - (0)_V \left( \frac{\partial S}{\partial V} \right)_T = (1)_V \left( \frac{\partial P}{\partial V} \right)_T - (1)_T \left( \frac{\partial P}{\partial T} \right)_V
\]
\[
\therefore \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{Maxwell’s II Relation}
\]
Maxwell’s III Thermodynamical relation:
Put \( x = S ; y = P \)
\[
\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad \text{Maxwell’s III Relation}
\]
Maxwell’s IV thermodynamical relation:
Put \( x = T ; y = P \)
\[
\left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P
\]
Maxwell’s V thermodynamical relation:
Put \( x = P ; y = V \)
\[
\left( \frac{\partial T}{\partial P} \right)_V = \left( \frac{\partial S}{\partial V} \right)_P - \left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial P}{\partial S} \right)_V = 1 \quad \Rightarrow \text{Maxwell’s V relation}
\]
Maxwell’s VI thermodynamical relation:
\( x = T ; y = S \)
\[
\left( \frac{\partial P}{\partial S} \right)_T = \left( \frac{\partial V}{\partial S} \right)_T - \left( \frac{\partial P}{\partial V} \right)_S \left( \frac{\partial V}{\partial P} \right)_T = 1
\]
\[
\text{Applications of Maxwell’s Thermodynamic relations:}
\]
1) Specific heat of Maxwell’s Thermodynamic relations:
\[
C_P = \left( \frac{\partial Q}{\partial T} \right)_P \quad \partial S = \frac{\partial Q}{\partial T}
\]
\[ C_P = \left( \frac{\partial S}{\partial T} \right)_P \]

2) Specific heat at constant volume

\[ C_V = \left( \frac{\partial Q}{\partial T} \right)_V \]

\[ C_P - C_V = T \left( \frac{\partial S}{\partial T} \right)_P - T \left( \frac{\partial S}{\partial T} \right)_V \]

Using Maxwell’s II relation the above equation becomes,

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

For a perfect gas

Equation of state is \( PV = RT \)

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V} ; \left( \frac{\partial V}{\partial T} \right)_P = -\frac{P}{V} \]

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

\[ = \frac{R}{V} \times \frac{R}{P} \times \frac{TR^2}{PV} \]

\[ C_P - C_V = \frac{TR^2}{RT} = R \]

\[ R = \text{Rydberg’s const.} \]

\[ \therefore \quad C_P - C_V = R \quad \rightarrow \text{Mayer’s Relation} \]

Vanderwaals gas:

\[ \left( P + \frac{a}{V^2} \right) = \frac{RT}{(V-b)} \]

\[ C_P - C_V = R \left( 1 + \frac{2a}{\sqrt[3]{VT}} \right) \]

**Joule Thomson cooling:**

When a gas is allowed adiabatically through a porous plug from the region of constant high pressure to the region at constant low pressure, the temperature of escaping gas changes. This is called as Joule Thomson effect.

The change of Temperature,

When +ve \( \rightarrow \) Heating

-ve \( \rightarrow \) Cooling

Zero \( \rightarrow \) No heating or cooling

\[ dT = \frac{V}{C_P} (\alpha T - 1) \] \( dp \) is the Equation for the change in Temperature due to Joule Thomson Effect.

Where, \( \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \)
Joule Thomson co-efficient (μ)
\[ \mu = \left( \frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[ \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial P} \right) - V \right] \]
\[ dT = \frac{V}{C_P} (\alpha T - 1) \, dp \]
Here dp is the fall in pressure and it is always a negative quantity.

Results of Joule Thomson Effect.
1) If (\( \alpha T - 1 \)) is +ve ; \( \alpha T > 1 \)
   and \( dT \) is Negative → Cooling Effect.
2) If (\( \alpha T - 1 \)) is zero ; \( \alpha T = 1 \)
   and \( dT \) is zero → No Cooling or Heating.
3) If (\( \alpha T - 1 \)) is -ve ; \( \alpha T < 1 \)
   and \( dT \) is Positive → Heating Effect.

For perfect gas, \( dT = 0 \)
\( \mu \) is zero.

For Vander Waals gas,
\[ \left( P + \frac{a}{V^2} \right) (V - b) = RT \]
1) \( V_c = 3b \)
2) \( T_c = \frac{8a}{27Rb} \)
3) \( P_c = \frac{a}{27b^2} \)

Critical co-efficient of a gas,
\[ \frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.667 \]

Temperature of inversion \( T_i = \frac{2a}{Rb} \)
Boyle’s Temp \( T_B = \frac{a}{Rb} \)
\[ \frac{T_i}{T_c} = \frac{27}{8} = 3.375 \]
\[ \therefore \frac{T_i}{T_c} = 6.75 \]

Temperature of inversion \( (T_i) \)
Temperature at which Joule Thomson Effect is zero and changes sign is known as Temperature of inversion.
\[ T_i = \frac{2a}{Rb} \]

Cases:
1) When \( T > T_i \) or \( \frac{2a}{RT} < b \) --- Heating Effect.
2) When $T < T_i \rightarrow$ Cooling Effect.
3) $T_i$ is different for different gases.
4) Adiabatic Expansion must result in fall of Temperature.
5) Adiabatic compression must result in increase in Temperature.

Thermodynamic potentials,
1) Integral Energy ($u$)
2) Helmholtz free energy or Helmholtz work function
   \[ F = u - TS \]
3) Enthalpy $H = u + Pv$
4) Gibb’s function $G = u + Pv - TS$

Integral Energy ($u$)
- $dQ = du + dw$ \hspace{1cm} \text{Isobaric – pressure constant}
- $du = dQ - dw$
- $du = dQ - Pdv$ \hspace{1cm} \text{Isochoric : Volume unchanged}
- $du = T ds - Pdv$

For an Adiabatic process, $dQ = 0$
As, $dQ = T ds$, $T ds = 0$

\[ du - Pdv \]

Enthalpy : Also known as Total heat
\[ H = u + Pv \]

Change in Enthalpy,
\[ dH = du + pdv + vdp \]
Now, $du = T ds - pdv$
\[ dH = T ds - pdv + pdv + vdp = T ds + vdp \]

For reversible isobaric process, $dp = 0$
\[ \therefore dH = T ds = dQ \]
\[ \therefore \] The change in Enthalpy is equal to the heat absorbed

Gibb’s function (G) or Gibb’s Free Energy
\[ G = u - TS + PV \]
\[ F = u - TS \]
\[ G = F + PV \]
This is the relation connecting Gibbs function and Helmholtz function

Enthalpy : $H = G + TS$
\[ = \text{Gibb’s free Energy + Latent heat} \]
\[ H = u + Pv \]
\[ u = H - P \]
Put $u$ value in Gibb’s Equation,
\[ G = u - TS + P \]
$$= H – P v – TS + PV$$

Gibb’s function $G$ remains constant in an Isothermal – Isobaric process.

**Relation between $C_p$, $C_v$ and $\mu$:**

$$C_p = (\frac{\partial H}{\partial T})_P$$

$$\mu = (\frac{\partial T}{\partial P})_H$$

$$C_v = (\frac{\partial V}{\partial T})_V – \text{doubt}$$

First Tds Equation is

$$\text{Tds} = C_v \text{dT} + (\frac{\partial P}{\partial T})_H \text{dv}$$

Second Tds Equation:

$$\text{Tds} = C_p \text{dT} - (\frac{\partial u}{\partial T})_P \text{dP}$$

**Phase Transition:**

**I order phase transition:**

The change of phase which takes place at constant temperature and pressure in which heat is either absorbed or evolved during the change of phase are called first order phase transitions.

* Here the entropy and density or volume changes.
* I order phase transition can be defined as the one in which the Gibb’s function with respect to pressure and temperature change discontinuously at the transition time.
* Clausius Clapyron Latent heat equation:

$$\frac{dp}{dt} = \frac{S_2 - S_1}{V_2 - V_1}$$

$$S_2 - S_1 = \Delta S = \frac{\delta Q}{T} = \frac{L}{T}$$

Where ‘$L$’ is the Latent heat of Vapourisation

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

This equation is called as the Clausius, Clapeyron latent heat equation or first order phase transition equation.

Eg: When heat is given to water at 100°C it changes from liquid to vapour state. The density of water is 1000kg/m$^3$.

* When there is a change of state from water to ice then volume, entropy density changes.

**Second order phase Transition:**

It can be defined as the phenomenon that takes place with no change in entropy and volume at constant temperature and pressure.

Eg: Transition of liquid Helium I to Helium II at $\lambda$ point (2.19k)

2) Transition of a ferro magnetic material to a paramagnetic material at Curie point.

3) Transition of a super conducting metal into an ordinary conductor in the absence of Magnetic field.

4) Order disorder Transition in chemical compounds and alloys
\[ K = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \rightarrow \text{Isothermal compressibility} \]

\[ \alpha = +\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \rightarrow \text{Volume coefficient of expansion} \]

\[ S_1 - S_2 = \frac{\delta Q}{T} \]

\[ S_1 - S_2 = L \rightarrow \text{Latent heat} \]

\[ S_1 - S_2 \Rightarrow S_1 - S_2 = 0 \]

For second order phase transitions, there is no change in entropy and volume.

\[ S_1 - S_2 \]

\[ dS_1 - dS_2 \]

\[ \frac{dp}{dT} = \frac{C_{P_2} - C_{P_1}}{TV (\propto_2 - \propto_1)} \]

\[ \frac{dp}{dT} = \frac{P_2 - C_{P_1}}{TV (\propto_2 - \propto_1)} \]

This is the equation for second order phase transition.

\[ \text{Also,} \]

\[ \text{Equation (1) and (2) are called as Ehrenfests equations.} \]

These Ehrenfests equation represents the condition of equilibrium between the two phases.

**Dulong and Petit's law**

"The atomic heat of all the Elements in the solid state is a constant"

\[ E = 3RT \]

The law can also be stated as, The product of the specific heat and the atomic weight of all the Elements in the solid state is a constant.

Whose value is 6.

Atomic heat = Specific heat x Atomic weight

Specific heat at constant volume

\[ C_v = \frac{dE}{dT} = \frac{d}{dT} (3RT) = 3R \]

\[ C_v = 3R \]

Where \( C_v \) is the atomic heat of substance whose value is 6.

\[ \therefore \text{Dulong and petits law is} \]

1) Atomic heat = 6
2) \( CV = 6 \)
3) \( \frac{dE}{dT} = 6 \)

Specific heat \( \rightarrow \) decreases with decrease in temperature
Specific heat at absolute zero \( \rightarrow \) Zero
Specific heat \( \rightarrow \) Increases with increase in Temperature
Atomic heat is Maximum at the value 6.
Production of low Temperature:

- The lowest Temperature corresponds to Ok (-273.16°C) is called the absolute zero temperature.
- Temperature upto - 65°C can be obtained with KoH and ice.
- With liquid helium boiling under normal pressure temperature of -268.9°C can be reached.
- By boiling liquid Helium under reduced pressure temperature of the order of 1K could be obtained (ie \( 1\) + OK = - 273.16°C +1 = - 272.16°C)
- With liquid helium isotope (He\(^3\)) boiling under reduced pressure a temperature of below 0.4K can be reached.
- Temperature below 0.4K can be reached by Adiabatic demagnetization method.
- Debye, Macdougall produced temperature below 1K with the help of galonium sulphate.

Adiabatic demagnetization
(1 Tesla = 10\(^4\) Gauss)

- The paramagnetic specimen (salt) is suspended in a vessel surrounded by liquid helium in Dewar flask.
- Liquid Helium is boiled under reduced pressure and it is placed in the dewar flask.

- The purpose of liquid Helium is to boil the substance.
- Liquid Hydrogen is placed below the Dewar flask so as to maintain the high temperature.
- The magnetic field provided when applied the temperature rises.
- When the magnetic field is removed the temp. reduces in paramagnetic substances.
- The Temp T is calculated by curie la

Curie law \( \chi = \frac{C}{T} \)
Haas was able to produce Temperature upto 0.002k using a double sulphate of potassium and aluminium.

According to Curie’s law

Intensity of magnetization, \( I \propto \frac{H}{T} \)

\( I = C \left( \frac{H}{T} \right) \)

\( C \) – Curie constant

I of I mole of paramagnetic substance,

\( M = IV \)

\( = C \left( \frac{H}{T} \right) V = CV \left( \frac{H}{T} \right) \)

Change in Temp, \( \Delta T = \frac{CV}{2CH_T} \left( H_2^2 - H_1^2 \right) \)

\( CH = \left( \frac{\partial Q}{\partial T} \right)_H \)

\( CH \) → Specific heat of a substance at constant magnetic field H.

If the magnetic field is reduced from \( H_1 = H \) to \( H_2 = 0 \). Then, change in Temperature \( \Delta T \)

\( = \frac{CV}{2CH_T} \left( 0 - H^2 \right) = \frac{-CV}{2CH_T} H^2 \).

\( \Delta T = \frac{-CV}{2CH_T} H^2 \).

* Temperature of paramagnetic substance decreases on decreasing the magnetizing field H.

* In the above \( \Delta T \), Greater in H (Initial field), lower is T (Initial temperature)

\( \therefore \) greater is the temperature fall \( \Delta T \).

* Cooling produced by Adiabatic demagnetization is explained using \( T - S \) (Temp-Entropy)

* During Adiabatic demagnetization the lower temp of the order of \( 10^{-4} \) can be reached.

* Measurement of very low temperature Human body = 36.98°C or 98.4°F.

* Helium vapour pressure thermometer is used to measure temp upto 0.7K

* For lower Temperature the graph between saturated vapour pressure and temp is extrapolated.

Normal graph – Intrapolated

Extended graph – Extrapolated

Phonons – Quantum of Energy.

* The energy of a lattice vibration or an Elastic wave is quantized and the quantum of this energy is termed as phonon.

* Sound waves – Acoustic phonons. Thermal vibrations – Thermally Excited phonons.

* Energy of phonon = \( \hbar \omega \).

\( \omega \) - Angular frequency of the mode of vibration.

* Total energy for ‘\( n \)’ number of phonon’s is,

\( E = \frac{\hbar \omega}{(e^{\hbar \omega/kT} - 1)} \)

\( \therefore E = n \hbar \omega \)
Here
\[ n = \frac{1}{(e^{\frac{\hbar \nu}{K T}} - 1)^{-1}} \]

* The number of phonons can be increased or decreased by raising or lowering the temp. respectively.
* Frequency of phonon waves are of the order \(10^4\) to \(10^{13}\) hz.
* As phonons are also termed as indistinguishable particle.

**Einstein’s theory of specific heat of solids:**

* Heat is radiated in the form of discrete particles called the photons.
* Each particle has the energy \(= h \nu\) where \(\nu\) is the frequency of heat radiation, \(h=\) Planck’s constant.
* When temp is raised the atoms execute SHM.
* Each Atom of solid has three degrees of freedom like monoatomic gas molecule.
* Mean energy per degree of freedom is ,
\[ \frac{h \nu}{e^{\frac{\hbar \nu}{K T} - 1}} \]
* Energy of each atom \(= \frac{3h \nu}{e^{\frac{\hbar \nu}{K T} - 1}} \)
* Energy content of 1 gram of atom of solid consisting of N atoms, \(E = \frac{3h \nu}{e^{\frac{\hbar \nu}{K T} - 1}} \)
* Atomic heat at constant volume,
\[ C_v = \frac{dE}{dT} = 3NK \frac{e^{\frac{h \nu}{K T}}}{(e^{\frac{h \nu}{K T}} - 1)^2} \left(\frac{h \nu}{K T}\right)^2 \]

* If \(\theta = \frac{h \nu}{K}\) \(\theta =\) Einstein Temp
NK = R - gas constant for a gram atom
* \(C_v = 3R \left[ \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2} \right] \) \(\theta = \) Einstein’s Temp

\[ \ln \theta = \frac{h \nu}{K} \quad ; \quad \text{Let} \; \theta = 1E \quad \theta = 3 \times 10^9 K \]
\[ K = 1.38 \times 10^{-23} \]

Then \(\theta E = \frac{h \nu E}{K} = \theta E = \) Einstein’s Temp
\(\nu E =\) Einstein frequency for that solid

* Equation (1) is the Einstein equation for the Atomic heat of the solid at constant volume.
* Atomic heat is a function of Temperature.
* At high Temp \(\left[ \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2} \right] \) becomes 1.
* \(\therefore C_v = 3R\) which resembles the Dulong and petit’s law.
* Atomic Heat decreases with the decrease in Temperature and at Absolute zero temp. tends to zero
  i.e. \(C_v = 0\)
* Experimental curves for Atomic heat and Temperature shows that the curves are same for all the substances.
Special case:

* At high temperature

\[
C_V = 3R \left[ \frac{e^{\frac{h\nu}{KT}}}{(e^{\frac{h\nu}{KT}}-1)} \left( \frac{h\nu}{KT} \right)^2 \right]
\]

\( \frac{h\nu}{KT} \) becomes small value

\[
\left( \frac{e^{\frac{h\nu}{KT}}}{(e^{\frac{h\nu}{KT}}-1)} \right)^2 = \left( \frac{h\nu}{KT} \right)^2
\]

By \( e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots \ldots \)

\[
= 1 + \frac{h\nu}{KT} + \frac{1}{2!} \left( \frac{h\nu}{KT} \right)^2 + \ldots \ldots
\]

\[
(e^{\frac{h\nu}{KT}} - 1)^2 = \left( 1 + \frac{h\nu}{KT} \right)^2.
\]

\[
C_V = 3R \left[ \frac{e^{\frac{h\nu}{KT}}}{(e^{\frac{h\nu}{KT}}-1)} \left( \frac{h\nu}{KT} \right)^2 \right]
\]

As \( T \to \infty \), \( \frac{h\nu}{KT} \to 0 \)

\[
C_V = 3R \left[ e^{\frac{h\nu}{KT}} \right] = 3R \left[ e^0 \right]
\]

\[
C_V = 3R(1) \text{ which resembles the Dulong and Petit's law with experimental value.}
\]

2) At low temperature:

As \( T \to 0 \), \( \frac{h\nu}{KT} \to \infty \).

\[
C_V = 0
\]

Thus the Atomic heat tends to zero as Temperature approaches to absolute zero.

* When \( T = 0 \); \( C_V = 0 \)

* \( T = \text{Max} ; C_V = 3R \)

\[
C_V \text{ ranges from 0 to } 3R
\]

* Atomic heat of different elements differs because of \( \nu E \) the characteristic frequency or Einstein's frequency.

* For elements like Copper, Aluminium, Iron etc. the atomic heat at low temp decreases more rapidly.

Debye's Theory of specific heat of solids

By Einstein Assumption:-

* Vibrations of all atoms are simple Harmonic and they all have one and the same frequency.

By Debye's assumption:-

* Any solid is capable of vibrating elastically in many different modes the frequency varying from one mode.
The number of modes of vibrating of solids is limited. When soild is subjected to continuous elastic vibrations, 2 kinds of vibrations are set up.

a) Longitudinal vibrations  
b) Transverse vibrations

Number of modes of longitudinal vibrations per unit volume with the frequency, \( \gamma \) and \( \gamma + d\gamma \) is

\[
\text{No. of modes} = \frac{4\pi^2 d \gamma}{C_e^3}
\]

\( C_e \) – Velocity of longitudinal vibrations.

In case of transverse vibrations,

\[
\text{No. of modes} = \frac{8\pi^2 d \gamma}{C_t^2} \quad \text{or} \quad \frac{4\pi^2 d \gamma}{C_t^3} \times 2
\]

Here \( C_t \rightarrow \) Velocity of Transverse vibrations.

Total No. of vibrations

\[
\int_0^V 4\pi v \left[ \frac{1}{C_{e3}} + \frac{1}{C_{t3}} \right] \gamma^2 d\gamma
\]

\( V \) – Volume, \( Y_m \rightarrow \) mode of frequency.

Total thermal energy for 1 gram atom of solid is

\[
E = \frac{9N}{Y_m^3} \int_0^\infty \frac{h \gamma^3 d\gamma}{e^{\frac{h \gamma}{kT}} - 1}
\]

Let characteristic Temp “0”

\[
\theta = \frac{h \gamma_m}{k} ; \quad Y_m = \frac{k \theta}{\mu}
\]

Specific heat of 1 gram atom at constant volume or Atomic heat is

\[
C_V = \frac{dE}{dT} = 3R \left[ 12 \left( \frac{T}{\theta} \right)^2 \int_0^{\frac{x}{\theta} e^{x-1} - \frac{1}{e^{x-1} - 1}} dx \right]
\]

The above equation is the Debye’s equation for atomic heat of a mono atomic solid.

\[
X = \frac{h \gamma}{kT} 
\]

\[
C_V = 3Rf \left( \frac{\theta}{T} \right)
\]

Where \( f \left( \frac{\theta}{T} \right) \) is the Deby’s function

* At high Temp, \( C_V = 3R \)
  * The atomic heat of all substances tends to a maximum value equal to 3R.
* At low Temperature near absolute zero.
  \[
  C_V = 77.94 \times 3R \left( \frac{T}{\theta} \right)^3.
  \]

\( C_V \propto T^3 \) -------- Deby’s \( T^3 \) law

* Deby’s \( T^3 \) law states that,

  At low temperature the atomic heat of solid is directly proportional to cube of the absolute temperature.

* Atomic heat is zero at absolute zero.

* The curves showing the variation of specific heat with temperature, is same for all the elements. Also the behavior of elements regarding the variation is similar.