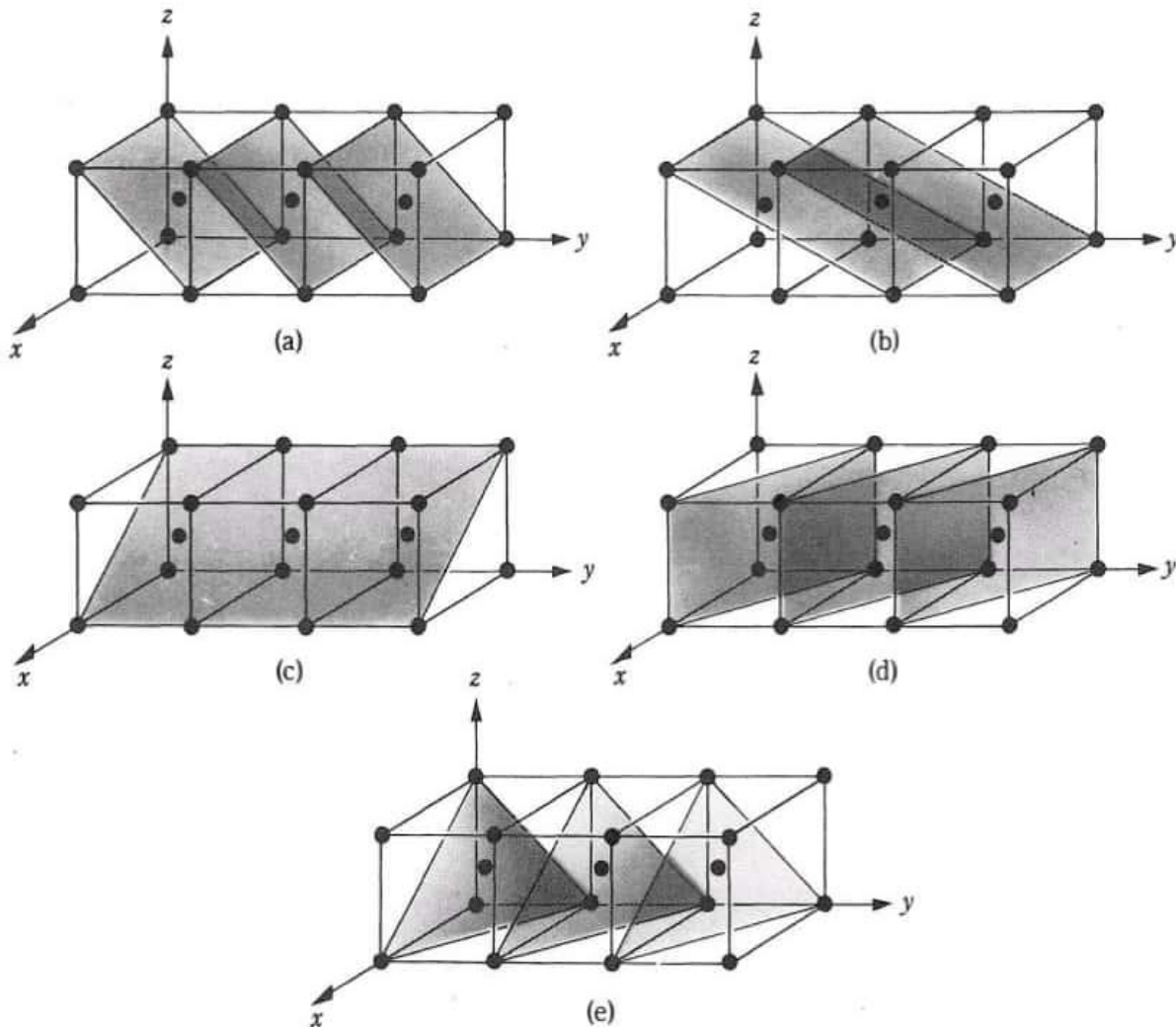


CRYSTAL PLANES:

Indexing of Planes

A helpful feature to remember is that the smaller the absolute value of h in the Miller index $\{hkl\}$, the more nearly parallel the set of planes is to the X-axis (the $\{h00\}$ planes are an exception). The same is true of k and the Y-axis, and l and the Z-axis. When $h = 0$, the planes intersect the X-axis at infinity, so the $\{0kl\}$ planes are parallel to the X-axis. Similarly, the $\{h0l\}$ planes are parallel to the Y-axis and the $\{hk0\}$ planes are parallel to the Z-axis.



Planes in the bcc lattice. (a) $0\ 1\ 1$ planes . (b) $0\ 1\ 2$ planes. (c) $1\ 0\ 1$ plane . (d) $1\ 1\ 0$ planes. (e) $1\ 1\ 1$ planes .

Note that the index 0 indicates that a plane is parallel to the corresponding axis.

Distance between lattice planes

Consider the $\{hk0\}$ planes of a square lattice built from a unit cell with sides of length a (Figure 1). The separation between the lattice planes is equal to the perpendicular distance from the $(hk0)$ plane to the origin. Expressions for the sine and cosine of the angle ϕ are found by considering the sides of the two right-angle triangles shown in the figure 1.

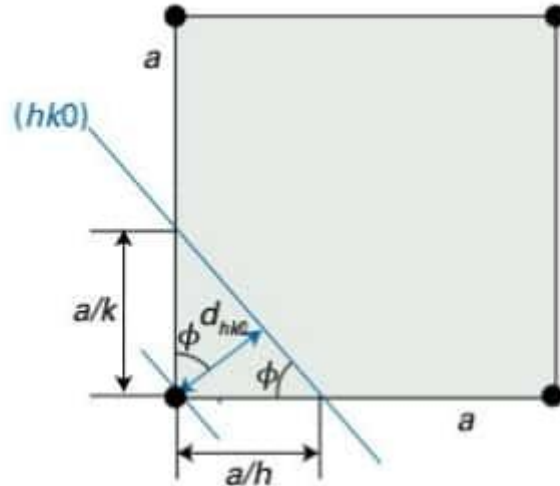


Figure 1

$$\sin \phi = \frac{d_{hk0}}{(a/h)} = \frac{hd_{hk0}}{a} \quad \text{and} \quad \cos \phi = \frac{d_{hk0}}{(a/k)} = \frac{kd_{hk0}}{a}$$

The length of the hypotenuse of the lower triangle is a/h because a Miller index h indicates that the plane intersects the a -axis at a distance a/h from the origin. Likewise, the hypotenuse of the upper triangle is a/k . Then, because $\sin^2 \phi + \cos^2 \phi = 1$, it follows that

$$\left(\frac{hd_{hk0}}{a}\right)^2 + \left(\frac{kd_{hk0}}{a}\right)^2 = 1$$

which can be rearranged by dividing both sides by d_{hk0}^2 into

$$\frac{1}{d_{hk0}^2} = \frac{h^2 + k^2}{a^2}$$

By extension to three dimensions, the separation of the $\{hkl\}$ planes, d_{hkl} , of a cubic lattice is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Or,

$$d_{hkl} = \frac{a^2}{\sqrt{h^2+k^2+l^2}} \text{ Separation of planes in Cubic lattice}$$

Where $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$

The corresponding expression for a general orthorhombic lattice (one in which the axes are mutually perpendicular, but not equal in length) is the generalization of this expression:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \text{ Separation of planes in Orthorhombic lattice}$$

Where $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

The corresponding expression for a general tetrahedral lattice is,

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \text{ Separation of planes in Tetrahedral lattice}$$

Where $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

Solved problem 1: Calculate the separation of (a) the {123} planes and (b) the {246} planes of an orthorhombic unit cell with $a = 0.82$ nm, $b = 0.94$ nm, and $c = 0.75$ nm.

Solution: For an orthorhombic lattice,

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\text{Or, } \frac{1}{d_{123}^2} = \frac{1^2}{0.82^2} + \frac{2^2}{0.94^2} + \frac{3^2}{0.75^2} = 22.0 \text{ nm}^{-2}$$

$$\text{Or, } d_{123} = 0.21 \text{ nm}$$

$$\text{Similarly, } d_{246} = 0.11 \text{ nm}$$

The ratios of the interplanar distance of different faces in the three types of cubic lattices

(i) Simple cubic lattice:

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

(ii) Body-centred cubic lattice:

$$d_{200} : d_{110} : d_{222} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} = 1 : 1.414 : 0.577$$

(iii) Face-centred cubic lattice:

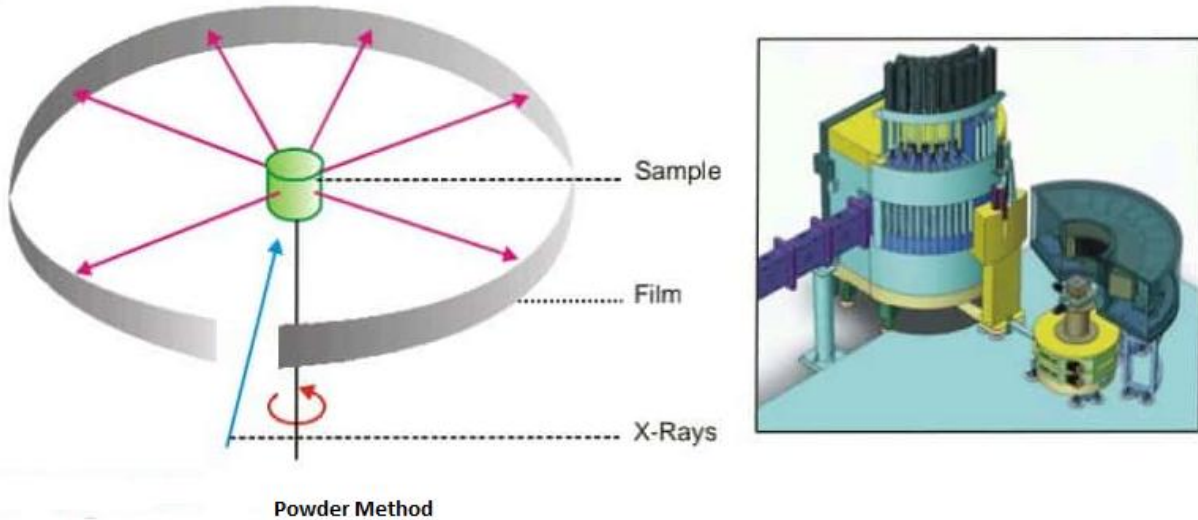
$$d_{200} : d_{220} : d_{111} = \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 1.154$$

MEASUREMENT OF DIFFRACTION ANGLE (θ)

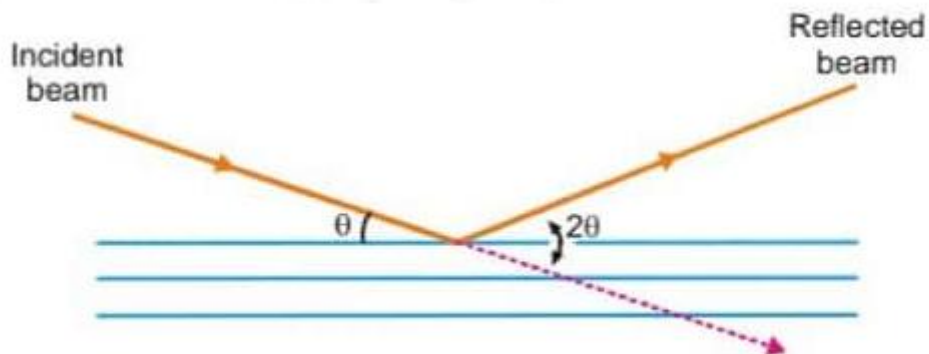
The measurement of diffraction angle, θ , required for Bragg equation can be done in the following method:
The powder method (Debye and Scherrer, 1916).

Powder Method

In this method the crystalline material contained in a capillary tube is placed in the camera containing a film strip (Figure below). The sample is rotated by means of a motor. The X-rays pass through the gap between the ends of the film.



The powdered sample contains small crystals arranged in all orientations. Some of these will reflect X-rays from each lattice plane at the same time. The reflected X-rays will make an angle 2θ with the original direction. Hence on the photo are obtained lines of constant θ . From the geometry of the camera, θ can be calculated for different crystal planes. The interplanar distance can be calculated using Bragg's equation from this angle, θ .



Angle made by the reflected beam with incident beam.

Structure of Sodium Chloride

Each sodium ion is surrounded by six chloride ions and each chloride ion is clustered by six sodium ions. The co-ordination number for this crystal lattice is six as required by simple cubic type. In this cubic system, the planes can be passed through the atoms having Miller indices (200), (220) or (111) and the relative spacings for the unit cell of a face-centred cubic lattice are $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ and $\frac{a}{\sqrt{3}}$ while it is $a, \frac{a}{\sqrt{2}}$ and $\frac{a}{\sqrt{3}}$ for simple cubic and $\frac{a}{2}, \frac{a}{\sqrt{2}}$ and $\frac{a}{2\sqrt{3}}$ for body-centred cubic lattice. For face-centred cubic lattice,

$$d_{200} : d_{220} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : 0.707 : 1.154 \dots\dots\dots(1)$$

The *first order* reflections from (200), (220) and (111) planes in case of sodium chloride was observed at the glancing angles 5.9° , 8.4° and 5.2° respectively. From Bragg equation $n\lambda = 2d\sin\theta$, we have

$$d = \frac{n\lambda}{2\sin\theta}$$

Since $n = 1$ and λ is the same in each case, the ratio of the spacings parallel to the three principal planes are

$$d_{200} : d_{220} : d_{111} = \frac{1}{\sin(5.9)} : \frac{1}{\sin(8.4)} : \frac{1}{\sin(5.2)} = \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.0906} = 1 : 0.705 : 1.137 \dots\dots\dots(2)$$

This agrees well the theoretical ratio for face-centred cubic lattice as shown in equation (1). Thus, on the basis of defraction data, **sodium chloride is found to have face-centred cubic lattice** which is shown in figure 2.

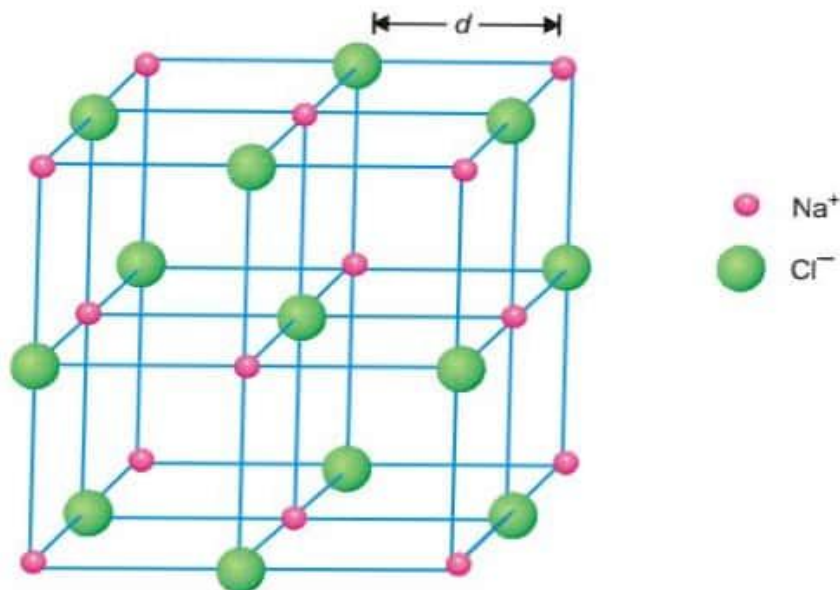


Figure 2

Structure of Potassium Chloride

Structure of KCl was studied by using Bragg's spectrometer. The intensities of ionization currents were determined for glancing angles and the current intensities were plotted against glancing angles. The first order spectrum from (100), (110) and (111) planes of KCl was observed at the glancing angles 5.38° , 7.61° and 9.38° respectively.

$$\therefore d_{100} : d_{110} : d_{111} = \frac{1}{\sin 5.38^\circ} : \frac{1}{\sin 7.61^\circ} : \frac{1}{\sin 9.38^\circ} = \frac{1}{0.0938} : \frac{1}{0.1326} : \frac{1}{0.1620} = 1 : 0.704 : 0.575$$

Now for a simple cubic lattice, $d_{100} : d_{110} : d_{111} = 1 : 0.707 : 0.575$ (Theoretical value)

It, therefore follows that **KCl has a simple cubic lattice.**

Solved problem 2:

Calculate the separation between the (a) 100 planes, (b) 111 planes, and (c) $12\bar{1}$ planes in a cubic lattice whose unit cell length is 529.8 pm.

Solution:

the separation between planes. For the 100 planes,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{1}{(529.8 \text{ pm})^2}$$

$$d = 529.8 \text{ pm}$$

For the 111 planes,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{3}{(529.8 \text{ pm})^2}$$

$$d = 305.9 \text{ pm}$$

For the $12\bar{1}$ planes,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{6}{(529.8 \text{ pm})^2}$$

$$d = 216.3 \text{ pm}$$

Solved problem 3:

Chromium crystallizes as a body-centered cubic structure with a density of $7.20 \text{ g}\cdot\text{cm}^{-3}$ at 20°C . Calculate the length of a unit cell and the distance between successive 110, 200, and 111 planes.

Solution:

First, find the length of a unit cell of chromium:

$$V = a^3 = \frac{m}{\rho} = \frac{2(51.996 \text{ g}\cdot\text{mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1})(7.20 \text{ g}\cdot\text{cm}^{-3})}$$

$$a = 288.4 \text{ pm}$$

For 110 planes:

$$\frac{1}{d_{110}^2} = \frac{1^2 + 1^2}{(288.4 \text{ pm})^2}$$

$$d_{110} = 203.9 \text{ pm}$$

For 200 planes:

$$\frac{1}{d_{200}^2} = \frac{2^2}{(288.4 \text{ pm})^2}$$

$$d_{200} = 144.2 \text{ pm}$$

For 111 planes:

$$\frac{1}{d_{111}^2} = \frac{1^2 + 1^2 + 1^2}{(288.4 \text{ pm})^2}$$

$$d = 166.5 \text{ nm}$$

Solved problem 4:

The observed Bragg diffraction angle of the second-order reflection from the 222 planes of a potassium crystal is $\theta = 27.43^\circ$ when X-radiation of wavelength $\lambda = 70.926$ pm is used. Given that potassium exists as a body-centered cubic lattice, determine the length of the unit cell and the density of the crystal.

Solution:

We can use the Bragg equation for a cubic unit cell

$$\sin^2 \theta = \frac{n^2 \lambda^2 (h^2 + k^2 + l^2)}{4a^2}$$
$$a = \left[\frac{12(70.926 \text{ pm})^2}{\sin^2 27.43^\circ} \right] = 533.4 \text{ pm}$$

The molar mass of potassium is $39.10 \text{ g} \cdot \text{mol}^{-1}$, and the body-centered cubic lattice has two atoms per unit cell. The density of the crystal is thus

$$\text{Density} = m/v = \frac{2(39.098 \text{ g} \cdot \text{mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1})(533.4 \times 10^{-10} \text{ cm})^3} = 0.8558 \text{ g} \cdot \text{cm}^{-3}$$

Solved problem 5:

The unit cell of topaz is orthorhombic with $a = 839$ pm, $b = 879$ pm, and $c = 465$ pm. Calculate the values of the Bragg X-ray diffraction angles from the 110, 101, 111, and 222 planes. Take the wavelength of the X-radiation to be $\lambda = 154.433$ pm.

Solution:

Use the Bragg equation for the first-order diffraction angle:

$$\lambda = 2 \left(\frac{d}{n} \right) \sin \theta = 2d \sin \theta$$

We now find d by substituting the values of hkl and a , b and c into the expression

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

The values for d , $\sin \theta$, and θ for each set of planes are tabulated below.

	d/pm	$\sin \theta$	θ
110	606.9	0.1272	7.309°
101	406.7	0.1899	10.94°
111	369.1	0.2092	12.08°
222	184.6	0.4183	24.73°

Specific Heat of Solid:

Coefficient of thermal expansion and compressibility of solids

The dependence of the volume of a solid on temperature at constant pressure can be expressed by the equation

$$V = V_0(1 + \alpha t) \dots\dots\dots(1)$$

where t is the celsius temperature, V_0 is the volume of the solid at 0°C , and α is the *coefficient of thermal expansion*. Any particular substance has different values of α in the solid state. The value of α is constant over limited ranges of temperature. For solids, α is always positive. If the data are to be represented with precision over a wide range of temperature, it is necessary to use an equation with higher powers of t :

$$V = V_0(1 + at + bt^2 + \dots\dots) \dots\dots\dots(2)$$

where a and b are constants.

In Eq. (1), V_0 is a function of pressure. Experimentally, it is found that the relation between volume and pressure is given by

$$V_0 = V_0^0 [1 - \kappa(P - 1)] \dots\dots\dots(3)$$

where V_0 is the volume at 0°C under one atmosphere pressure, p is the pressure in atmospheres, and κ is the *coefficient of compressibility*, which is a constant for a particular substance over fairly wide ranges of pressure. The value of κ is different for each solid substance. The necessary condition for mechanical stability of a substance is that κ must be positive.

According to Eq. (3) the volume of a solid decreases linearly with pressure. The values of κ for solids are extremely small, being of the order of 10^{-6} to 10^{-5} atm^{-1} . If we take $\kappa = 10^{-5}$, then for a pressure of two atmospheres, the volume of the condensed phase is, by Eq.(3), $V = V_0^0 [1 - 10^{-5}(1)]$. The decrease in volume in going from 1 atm to 2 atm pressure is 0.001 %. Because moderate changes in pressure produce only very tiny changes in the volume of solids, it is often convenient to consider them to be incompressible ($\kappa = 0$) in the first approximation.

Heat capacity of solids

The heat capacity, C , of a system is the ratio of the heat added to the system, or withdrawn from the system, to the resultant change in the temperature:

$$C = \Delta Q / \Delta T = dQ / dT \text{ [J/deg]}$$

Usually C is given as *specific heat capacity*, c , per gram or per mol. Heat capacity is a measure of the ability of the material to absorb thermal energy.

Dulong – Petit’s law

The constant value of the heat capacity of many simple solids is called Dulong – Petit’s law. In 1819 Dulong and Petit found experimentally that for many solids at room temperature, $c_v \approx 3R = 25 \text{ JK}^{-1}\text{mol}^{-1}$.

Limitations:

Some solid elements show large deviations from this rule and the specific heat capacity changes with change in temperature.

Einstein's theory of heat capacities

Einstein considered a model in which atoms in a solid vibrate independently of each other. Each vibration can be considered as a simple harmonic oscillator. Since oscillation is independent in the x, y and z directions, for N atoms there are 3N independent oscillators, each vibrating independently at frequency ν_ϵ .

The energy levels of the harmonic oscillators are given by

$$\epsilon_v = h\nu_\epsilon \left(v + \frac{1}{2}\right), \quad v = 0, 1, 2, \dots$$

Assuming the oscillators are in thermal equilibrium at temperature T, the partition function (Z) for a single oscillator is

$$Z = \sum_{v=0}^{\infty} e^{-\beta\epsilon_v} = \sum_{v=0}^{\infty} e^{-\beta h\nu_\epsilon \left(v + \frac{1}{2}\right)} = e^{-\frac{x}{2}} \sum_{v=0}^{\infty} e^{-xv} = \frac{e^{-\frac{x}{2}}}{1 - e^{-x}} \quad \text{where, } x = \beta h\nu_\epsilon.$$

In the above, we have used the fact that $\sum_{n=0}^{\infty} X^n = \frac{1}{1-X}$. [In our case, $X = e^{-x}$]

We can use the partition function to find the mean energy of oscillator

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \left[-\frac{x}{2} - \ln(1 - e^{-x}) \right] = \frac{1}{2} h\nu_\epsilon + \frac{h\nu_\epsilon}{e^{\beta h\nu_\epsilon} - 1}$$

The energy of the 3N oscillators in the N-atom solid is

$$E = 3N\langle E \rangle = 3N \left[\frac{1}{2} h\nu_\epsilon + \frac{h\nu_\epsilon}{e^{\beta h\nu_\epsilon} - 1} \right] = 3N \left[\frac{1}{2} h\nu_\epsilon + \frac{h\nu_\epsilon}{e^{\frac{h\nu_\epsilon}{k_B T}} - 1} \right] \quad (\text{As, } \beta = \frac{1}{k_B T})$$

The heat capacity at constant volume is therefore

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3N \left(\frac{\partial E}{\partial \beta} \right)_V \left(\frac{\partial \beta}{\partial T} \right)$$

$$\text{Or, } C_V = 3Nk_B \left(\frac{h\nu_\epsilon}{k_B T} \right)^2 \frac{e^{\frac{h\nu_\epsilon}{k_B T}}}{\left(e^{\frac{h\nu_\epsilon}{k_B T}} - 1 \right)^2}$$

$$\text{or, } C_V = 3R \left(\frac{h\nu_\epsilon}{k_B T} \right)^2 \frac{e^{\frac{h\nu_\epsilon}{k_B T}}}{\left(e^{\frac{h\nu_\epsilon}{k_B T}} - 1 \right)^2} \dots\dots\dots(1)$$

Equation (1) is known as Einstein's equation.

$$\text{or, } C_V = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1 \right)^2} \dots\dots\dots(2)$$

Where $\theta_E = \frac{h\nu_\epsilon}{k_B}$ is known as 'Einstein temperature', which is different for each solid, and reflects the rigidity of the lattice.

From equation (2)

$$C_V = 3R \frac{x^2 e^x}{(e^x - 1)^2}$$

$$\text{Where, } x = \frac{h\nu_\epsilon}{k_B T}$$

At the high temperature limit, when $T \gg \theta_E$, $x \ll 1$ and the Einstein heat capacity reduces to $C_V = 3R$ (the Dulong and Petit law). [prove by setting $e^x \sim 1+x$ in the denominator]

At the low temperature limit, when $T \ll \theta_E$, $x \gg 1$ and $C_V = 3R(\theta_E/T)^2 e^{-\theta_E/T}$, which goes to 0 as T decreases. [Prove by setting $e^x - 1 \sim e^x$ in the denominator for large x].

Limitations:

At lower temperatures, the calculated values (from Einstein equation) fall more rapidly than the experimental values. This disagreement is due to Einstein's assumption that all the atoms oscillate with the same frequency, ν_ϵ , whereas in fact they oscillate over a range of frequencies from zero upto a maximum value.

Debye's T^3 law:-

Debye (1912) developed a modified equation which gave a very satisfactory agreement with experiment over the entire temperature range. He suggested that a solid is to be assumed as an elastic body and the vibrations of all the $3N$ atoms in a gram-atom of a monoatomic solid are not all identical but are distributed over a range of frequencies from zero upto a maximum frequency, ν_D which is characteristic of a solid. According to Debye equation,

$$C_V = 3NK_B \left(\frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \right)$$

where, $x = \frac{h\nu}{K_B T}$ and $x_D = \frac{h\nu_D}{K_B T} = \frac{\Theta_D}{T}$.

The Debye heat capacity depends only on the Debye temperature Θ_D . where, $\Theta_D = \frac{h\nu_D}{K_B}$.

(i) At high temperature ($T \gg \Theta_D$, $x_D \ll 1$), we may rewrite the integrand as follows:

$$\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4}{(e^x - 1)(e^x - 1)} = \frac{x^4}{2(\cosh(x) - 1)} = \frac{x^4}{2\left(\frac{x^2}{2!} + \frac{x^4}{4!} + \dots\right)}$$

Retaining only the x^2 term in the denominator gives,

$$C_V = 3NK_B \left(\frac{3}{x_D^3} \int_0^{x_D} x^2 dx \right) = 3NK_B = 3R$$

(ii) At low temperature limit ($T \ll \Theta_D$, $x_D \gg 1$), we note that the integrand tends towards zero rapidly for large x . this allows us to replace the upper limit by ∞ and turn the integral into a standard integral,

$$\therefore C_V = 3NK_B \left(\frac{T}{\Theta_D} \right)^3 \left(3 \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx \right)$$

$$\therefore C_v = \frac{12}{5} \pi^4 N K_B \left(\frac{T}{\theta_D} \right)^3$$

For a given substance, at ^{very} low temperature,

$$C_v = \frac{464 \cdot 6}{\theta_D} T^3 = \alpha T^3 \quad \text{--- (1)}$$

The equation (1) is known as Debye's T^3 law.